

Emerging polymer-based electrolytes for coordination-mediated ion transport and interface stabilization in solid-state lithium batteries

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ABSTRACT

All-solid-state lithium batteries are pivotal for next-generation energy storage, yet their development is hampered by the intrinsic limitations of polymer-based electrolytes, such as low ionic conductivity and interfacial instability. The coordination chemistry of ions—particularly lithium ion and the corresponding anions—with functional groups governs ion transport and interface regulation in polymer electrolytes. Despite considerable advances in this field, systematic analysis from a coordination chemistry perspective remains notably scarce. This review aims to establish a coherent framework that connects molecular-level design to macroscopic electrolyte properties via coordination chemistry. Specifically, it outlines the ion-coordination mechanisms in conventional polyether-based electrolytes and advances to discuss modern polymer design strategies that modulate ion transport through alternative coordination chemistries, including the use of competitive units (e.g., heterometallic ions, organic cations), polymer functionalization with charged/zwitterionic groups, and solvation structure engineering derived from high-concentration electrolytes. Furthermore, the latest and most representative polymer-based electrolyte systems from the perspective of their coordination structure and interface behavior are organized and presented, highlighting their unique merits and underlying principles. Finally, a forward-looking perspective is articulated, exploring promising directions such as precise electrolyte customization for specific battery configurations, on-demand synthesis of functional polymers, and the development of new coordination-assisted interfacial layers. Serving as a bridge between theory and practice, this review consolidates key insights to guide the development of next-generation polymer-based electrolytes for solid-state batteries.

1. Introduction

The accelerating global energy transition and widespread electrification are driving the urgent need for efficient and safe energy storage technologies. Lithium-based batteries, which underpin contemporary energy storage and power systems, are the focus of intense research and technological innovation [1–5]. Among next-generation candidates,

all-solid-state lithium batteries (ASSLB) are poised to supersede conventional lithium-ion (Li^+) systems by overcoming their inherent limitations in energy density and safety [6–8]. This advantage is particularly decisive when pairing with high-capacity lithium metal anodes—a combination notoriously challenged by the flammability of liquid electrolytes. The solid-state electrolyte, serving as the core component of ASSLB, is critical to overall battery performance [7,9,10].

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Polymer-based electrolytes, particularly, have attracted considerable interest due to their favorable processing compatibility and mechanical properties. However, their practical deployment and commercialization are still hindered by intrinsic limitations, including low ionic conductivity, unsatisfactory lithium-ion transference number (t_{Li^+}), and poor interfacial stability [11–13].

To address these challenges, several strategies have been explored. These include the introduction of various plasticizers to form gel, semi-solid, or quasi-solid electrolytes, where the plasticizers facilitate salt dissociation and ion transport while modulating the lithium-ion solvation structure via coordination with polymer chains and other components [14–17]. Another widely adopted approach involves incorporating inorganic fillers to suppress polymer crystallization, which not only enhances chain segment mobility but also directly or indirectly participates in Li^+ coordination to improve mechanical and electrochemical properties [18,19]. The molecular design of polymer architectures has also gained attention—for instance, through hyper-branched or supramolecular polymers that reduce crystallinity and tailor lithium-ion coordination environments [20,21]. More recently, competitive coordination strategies involving hetero-metal ions or organic cations have emerged [22–26]. These can expand interchain spacing and lower the migration energy barrier for Li^+ , and importantly, enable the decoupling of Li^+ transport from polymer segmental motion, leading to room-temperature ionic conductivity exceeding $10^{-3} \text{ S cm}^{-1}$ in all-solid-state polymer-based electrolytes. In contrast to traditional single-ion conductors where strongly interacting anionic groups often result in high Li^+ migration barriers, the introduction of cationic or zwitterionic groups offers a new perspective for coordination chemistry design [27,28]. Cationic groups can immobilize bulky anions, while anionic groups interact weakly with small Li^+ , significantly enhancing the t_{Li^+} . Inspired by high-concentration and localized high-concentration electrolytes in liquid systems, the simultaneous incorporation of weak and strong coordinating groups/segments into polymer matrices can create an anion-rich solvation structure, facilitating Li^+ transport and promoting the formation of stable inorganic-rich interphases [29–31].

These advances collectively underscore that the rational design of Li^+ coordination environments and solvation structures lies at the heart of developing high performance polymer-based electrolytes. While coordination chemistry has increasingly been recognized as a fundamental lever for tuning ionic transport and interfacial properties, the field still lacks a systematic and critical overview that connects molecular-scale mechanisms to macroscopic electrolyte performance. Such a gap hinders the transition from empirical discovery to principled design. To address this need, this review provides a comprehensive analysis of the coordination chemistry underpinning polymer-based electrolyte behavior. We begin by elucidating coordination and transport mechanisms in classical polyether-based systems, then extend more discussion to advanced electrolyte designs involving competitive coordination units, charged polymer backbones, and engineered solvation networks. Key characterization techniques and structure–property relationships are critically examined. Finally, we offer forward-looking perspectives on the application of precision coordination chemistry in designing polymer-based electrolyte for next-generation solid-state batteries, aiming to establish a foundational framework that bridges fundamental insight and practical innovation.

2. Coordination that governs ion and interface

Polymer-based electrolytes are regarded as one of the most promising solution for next-generation high-safety lithium-based batteries [32,33]. Research on polymer-based electrolytes originated in 1973 when Fenton et al. discovered that PEO complexes with alkali metals could conduct ions [34]. Since then, polymer-based electrolytes have garnered widespread attention and intensive research. With the development of solid-state batteries, the inconsistent definitions of

all-solid-state and semi-solid-state batteries have led to market confusion. In response, the China Society of Automotive Engineers has taken the lead in proposing a unified benchmark for the requirements of ASSLB: the sample must exhibit a weight loss rate of $<1\%$ after being subjected to vacuum drying at 120°C for 6 h. Based on this criterion, polymer-based electrolytes can also be classified according to their residual liquid content (Fig. 1).

Based on their physical states and microstructures, polymer-based electrolytes can be broadly classified into all-solid-state polymer electrolytes (SPE), quasi-solid polymer electrolytes (QSPE), gel polymer electrolytes (GPE), and composite polymer electrolytes (CPE) (Fig. 2). Each type of these polymer-based electrolytes possesses distinct advantages and disadvantages and is suitable for specific electrochemical environments. In these polymer-based electrolyte systems, coordination interactions generally serve as the "scheduling center" for ion transport. Through dynamic coordination and dissociation between polymer chains, additives, plasticizers, inorganic fillers, and Li^+ , ion migration channels are constructed and regulated, thereby determining the core performance of the electrolytes. This section will elaborate on the specific applications and design strategies of coordination mechanisms in different systems.

2.1. Ion transport via coordinated dynamics in SPE

SPE, also known as ion-conducting polymers, have emerged as one of the most promising electrolyte systems due to the exceptional safety and processability. In 1983, Michel Armand reported a PEO-alkali metal salt conductive complex that exhibited an ionic conductivity of up to $10^{-5} \text{ S cm}^{-1}$ within the temperature range of $40\text{--}60^\circ\text{C}$ and demonstrated excellent film-forming properties, making it suitable for use as an electrolyte in lithium-ion batteries (LIB) [35,36]. Since the ion transport in SPE relies on the polymer matrix, a thorough understanding of the coordination interactions between polymer chains and Li^+ is crucial for elucidating their conduction mechanisms and optimizing their performance. As illustrated in Fig. 3, Li^+ exhibit multiple transport mechanisms within SPE, among which the "chain motion-facilitated ion transport" mechanism represents the most classic coordination model [37]. Li^+ can coordinate with polar functional groups on polymer segments, such as ether oxygen (EO), carbonyl ($\text{C}=\text{O}$), and nitrile ($-\text{CN}$) groups, and is transported along with the motion of these segments [38]. It is worth noting that the molecular weight and chain length of the polymer matrix play a critical role in Li^+ transport efficiency and coordination dynamics [39,40]. Higher molecular weight polymers typically exhibit reduced segmental mobility and increased glass transition temperature (T_g), which would hinder Li^+ transport. In contrast, lower molecular weight systems or shorter chains provide enhanced segmental motion but may weaken the stability of coordination environments. These effects suggest that polymer chain structure significantly influences the coupling between segmental dynamics and ion transport behavior. In addition to this, other transport modes include Li^+ moving along polymer chains through complexation-decomplexation-recomplexation (intrachain transport) and hopping between different polymer chain segments (interchain transport) [41,42]. A detailed analysis of the coordination chemistry

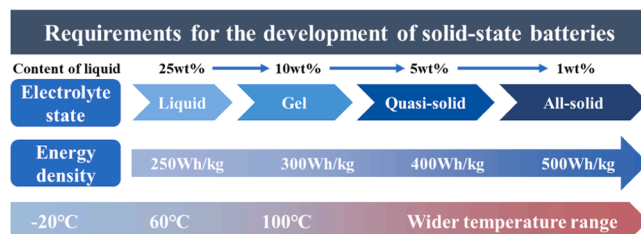


Fig. 1. Requirements for the development of solid-state batteries (data from Institute of Physics CAS).

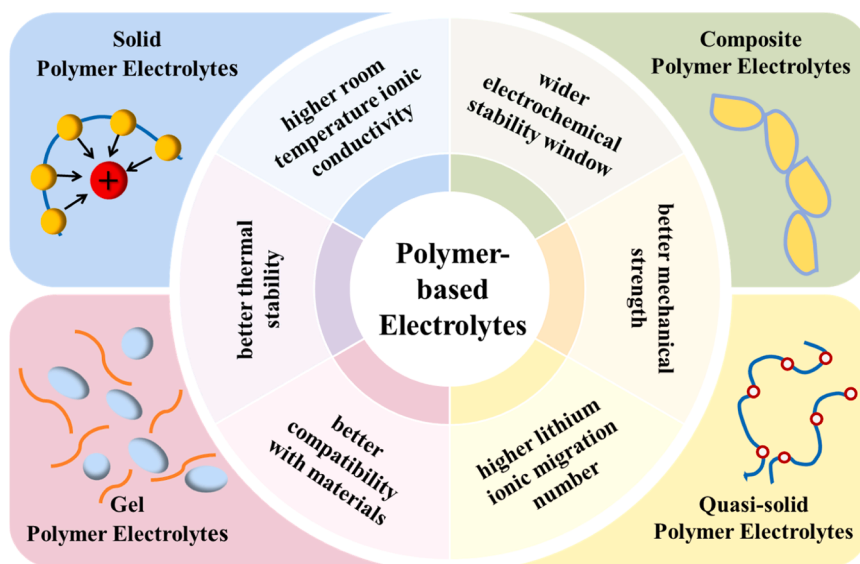


Fig. 2. Common polymer-based electrolytes.

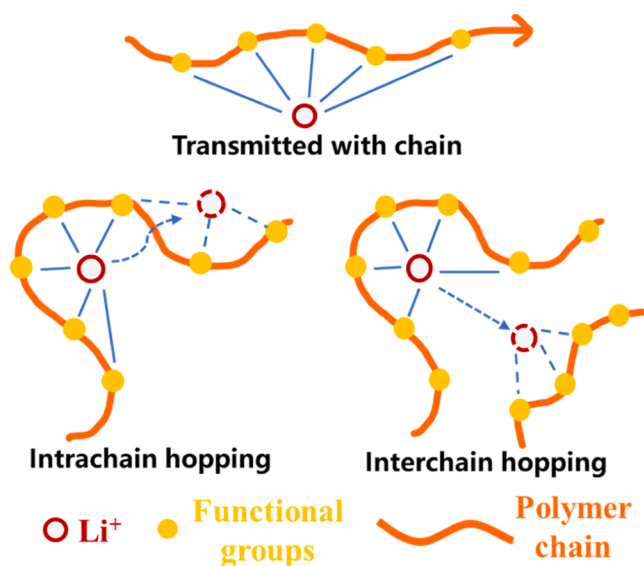


Fig. 3. Li^+ transport mechanisms in SPE, including chain-assisted transmit, intrachain hopping, and interchain hopping processes. Specifically, Li^+ migration occurs through dynamic coordination with functional groups along polymer chains, where segmental motion enables ion transport along the chain, while coordination-decoordination processes facilitate ion hopping within and between polymer chains.

between functional groups and Li^+ (e.g., coordination number, binding energy) is more conducive to achieving the desired electrochemical performance. In the case of the "chain motion-facilitated ion transport" mechanism, excessively low coordination strength can lead to incomplete dissociation of lithium salt, preventing effective transport of Li^+ along the chains. Conversely, for intrachain transport, the coordination strength must not be excessively high; otherwise, Li^+ cannot rapidly decouple to enable hopping between adjacent sites [43,44]. Furthermore, employing molecular dynamics simulations to investigate how the "formation-dissociation" processes of dynamic coordination bonds integrate with the irregular thermal motions of polymer chains to collectively govern ion migration is also an effective approach for studying the application of coordination mechanisms in polymer-based electrolytes [45].

2.2. Liquid-solid synergy via coordination in QSPE

Despite significant progress achieved through molecular design to optimize the coordination environment, the inherent issues of low room-temperature conductivity and high interfacial impedance in SPE remain unresolved. In 1975, Feuillade et al. attempted to introduce organic plasticizers into the polymer-lithium salt binary system, aiming to overcome performance bottlenecks by adding small amounts of liquid components or plasticizers to modify the coordination environment. This approach gradually evolved into the QSPE system [46,47]. In such electrolytes, the addition of plasticizers alters the coordination environment, rendering the ion transport mechanism more complex. He et al. systematically elucidated the Li^+ conduction mechanism in QSPE through multi-spectral characterization combined with first-principles calculations [48]. By analyzing the classic system of lithium salt (lithium bis(trifluoromethanesulfonyl)imide, LiTFSI)-polymer matrix (Poly(vinylidene fluoride-hexafluoropropylene), PVDF-HFP)-plasticizer/solvent (Tetraethylene glycol dimethyl ether, G4), various research characterizations indicated that Li^+ preferentially coordinates with G4 and exhibits negligible interaction with PVDF-HFP. The internal structure of QSPE is not a homogeneous solution but rather a microscopically phase-separated structure: a portion of G4 is immobilized by polymer chains through strong interactions, forming a robust network skeleton that provides mechanical strength, while the remaining G4 remains in a free state, accumulating in the pores of the polymer network. LiTFSI dissolves in these free, unbound G4 molecules. Essentially, Li^+ conduction occurs in regions of "high-concentration liquid electrolytes" separated by the polymer network, resembling the transport mechanism of liquid electrolytes (vehicular transport) rather than the traditional solid-state mechanism involving polymer chain motion. Of course, Li^+ conduction does not exclusively follow a liquid electrolyte mechanism in all QSPE systems. Zhang et al. constructed an in-situ polymerized QSPE, still utilizing the G4-lithium salt combination but selecting cross-linked poly(trifluoroethyl acrylate) as the polymer matrix [49]. This design aimed to disrupt the G4- Li^+ chelation solvation cage that hinders Li^+ migration by enabling $\text{C}=\text{O}$ to compete with the EO units of G4 for Li^+ coordination [50]. In this system, the Li^+ transport mechanism shifted to a dual-mechanism synergy: a portion of Li^+ is still carried by G4 solvent molecules, while another portion undergoes hopping transport between $\text{C}=\text{O}$ on the polymer chains.

Generally speaking, for traditional plasticizers (e.g., carbonates) and novel plasticizers like ionic liquids (IL), the polar functional groups (e.g., $\text{C}=\text{O}$, $-\text{CN}$) in their molecules compete with polymer chains (e.g., the

EO units in PEO) for coordinating with Li^+ [51]. This competition renders chain motion no longer the sole pathway for ionic conduction. On one hand, this competitive effect weakens the interaction between Li^+ and polymer chains, facilitating easier dissociation and migration of ions. On the other hand, the plasticizers themselves can also serve as media for ion transport, forming low-viscosity "ion highways" within the polymer network [52]. It can be said that the key to preparing an excellent QSPE lies in balancing the coordination competition between the polymer and the plasticizer for Li^+ , so as to achieve high-speed ion transport while preventing plasticizer exudation and maintaining the mechanical strength of the electrolyte. As the plasticizer content further increases, the morphology and conduction mechanism of the system undergo certain changes. The polymer network transitions from a continuous phase to a three-dimensional skeleton permeating the liquid electrolyte, entering the realm of the GPE, where the coordination effect exhibits liquid-solid biphasic synergistic characteristics.

2.3. A coordination bridge between liquid and solid in GPE

QSPE and GPE are not entirely equivalent concepts, yet they exhibit significant overlap in composition, physical state, and applications, often being used interchangeably. Fig. 4 illustrates the common transport modes of Li^+ in QSPE and GPE. Strictly speaking, GPE represent a typical form of QSPE but place greater emphasis on its "gel" structure. GPE combine the high ionic conductivity of liquid electrolytes with the mechanical strength and stability of solid electrolytes. The abundant liquid electrolyte phase within GPE provide the primary channels for ion transport, while the polymer skeleton serves a dual role as a "coordination regulator" and structural support [53].

In liquid electrolytes, solvent molecules (e.g., EC/DMC) preferentially coordinate with Li^+ to form a solvation sheath, enabling rapid ion migration. However, the polymer skeleton is not entirely inert; its polar sites engage in weak interactions (e.g., dipole-dipole forces) with solvated ions or partially replace solvent molecules within the coordination sheath. Such interactions effectively stabilize the electrolyte interface, suppress side reactions of solvent molecules, and regulate Li^+ deposition behavior. Additionally, for physically or chemically cross-linked polymer networks, their chain motions also adhere to a coordination-dissociation mechanism, providing auxiliary pathways for ion transport. Therefore, the key to optimizing GPE performance lies in the molecular chain design of the polymer matrix, as well as in optimizing the selection of solvents and lithium salts to achieve optimal coordination synergy [54]. Zhai et al. developed a GPE for high-voltage lithium metal batteries (LMB) by progressively engineering the solvation structure through synergistic incorporation of three functional additives [55]. Using poly(ethylene glycol) diacrylate (PEGDA) and poly(1,3-dioxolane) as the polymer matrix, they sequentially introduced LiNO_3 , perfluoropolyether nitrile, and lithium bis(fluorosulfonyl)imide (LiFSI). With the ordered addition of different additives, the

coordination between Li^+ and polar solvents gradually weakened. The Li^+ transport mechanism transitioned from collective movement of Li^+ with the entire solvation sheath to dominant hopping transport of Li^+ between different coordination sites. Consequently, the t_{Li^+} increased from 0.18 to 0.92, while the room-temperature ionic conductivity rose from $1.54 \times 10^{-3} \text{ S cm}^{-1}$ to $2.58 \times 10^{-3} \text{ S cm}^{-1}$.

Although GPE have successfully integrated the advantages of both liquid and solid phases, there remains significant room for improvement in their mechanical strength and dendrite resistance. The introduction of inorganic fillers into the polymer matrices to construct CPE offers the potential to leverage active sites on the filler surfaces for "multiphase coordination."

2.4. Synergy beyond the matrix in CPE

CPE significantly enhance the overall performance of electrolytes by incorporating active or inert fillers into the polymer matrix [56,57]. The introduction of inorganic fillers is far from a simple physical blending process, instead, it profoundly alters the coordination chemistry environment within the system. The coordination interactions extend to a multiphase, multidimensional synergy among fillers-ions-polymers, significantly expanding the design dimensions of coordination mechanisms.

Fillers with Lewis acidity (e.g., LLZO, LLTO, Al_2O_3) feature unsaturated metal sites on their surfaces that can form strong coordination with anions (e.g., TFSI^-) in the electrolyte. This interaction effectively immobilizes the anions, leading to a substantial increase in the t_{Li^+} [58,59]. Secondly, functional groups on the filler surface, such as hydroxyl (-OH) groups, can form hydrogen bonds and other interactions with polar groups on polymer chains. This suppresses crystallization of polymer chains, enhances segmental mobility, and indirectly promotes the coordination-dissociation process [60]. More importantly, at the filler/polymer interface, a space charge layer or an ion-permeable network with unique coordination structures and rapid ion transport kinetics is formed [61]. Different type of fillers (inert oxides, fast ion conductors, framework materials, etc.) play distinct but critical roles in constructing ion transport pathways. Song et al. synthesized $\text{La}(\text{OH})_3$ nanofibers with oxygen vacancies and functionalized their surfaces by introducing $-\text{NH}_2$ groups. The resulting $\text{La}(\text{OH})_3\text{-NH}_2$ was incorporated into a PEO/LiTFSI matrix to fabricate the CPE [62]. Oxygen vacancies as the Lewis acid sites, coordinate with the O or F atoms in TFSI^- anions, thereby immobilizing them. The $-\text{NH}_2$ groups provide lone pair electrons for coordination with Li^+ , promoting Li salt dissociation. Additionally, they form hydrogen bonds with O atoms in the PEO chains, suppressing PEO crystallization. Interconnected ion transport channels are formed between $\text{La}(\text{OH})_3\text{-NH}_2$ and the polymer chains, facilitating rapid Li^+ migration.

It should be noted that the general definition of CPE involves the introduction of fillers into polymer-based electrolytes without the

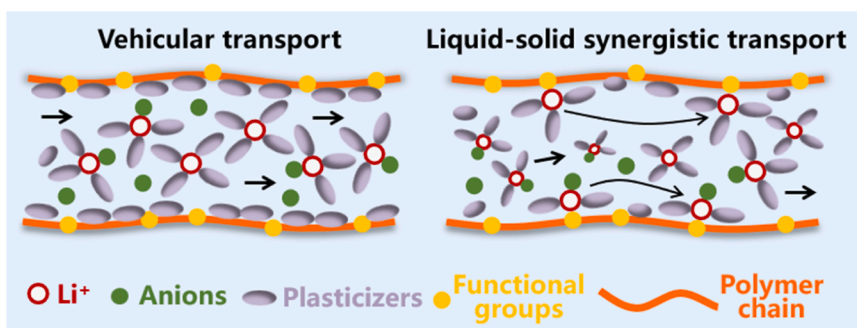


Fig. 4. Two classical Li^+ transport mechanisms in QSPE and GPE, highlighting the differences between vehicular transport and liquid-solid synergistic transport. In the vehicular transport mode, Li^+ primarily migrates with solvated species within the liquid phase (plasticizers), accompanied by free anions. In contrast, the liquid-solid synergistic mechanism involves both liquid phase ion transport and through coordination interactions with polymer functional groups.

addition of extra solvents or plasticizers. However, based on current research, although CPE can enhance the room-temperature ionic conductivity of SPE, the improvement is often limited. For instance, Li et al. reported a certain CPE with a room-temperature ionic conductivity of merely $7.7 \times 10^{-6} \text{ S cm}^{-1}$ [63]. Therefore, the introduction of plasticizers into CPE is also a commonly employed strategy, which complicates the coordination mechanism, allowing such systems to be termed as composite gel polymer electrolytes (CGPE). In CGPE, the incorporation of plasticizers such as succinonitrile (SN) or IL introduces additional coordination sites and modulates the local solvation structure. The polar groups in plasticizers (e.g., $-\text{CN}$ in SN) can coordinate with Li^+ , weakening the interaction between Li^+ and polymer chains or anions, thereby facilitating ion dissociation and mobility. Moreover, the coexistence of fillers and plasticizers creates a more complex interfacial coordination network. In such systems, fillers often act as Lewis acid sites to trap anions or as structural modifiers to suppress polymer crystallization, while plasticizers enhance segmental motion and form continuous ion-transport pathways via their own fluidity and coordination diversity. Ye et al. fabricated a CGPE based on PEGDA [64]. For the filler, aluminum ethoxide nanowires ($\text{Al}(\text{EtO})_3$), which possess abundant unsaturated coordinated Al atoms (Lewis acid sites), were selected. A mixture of carbonate-based solvents was used as the plasticizer. The Al atoms in $\text{Al}(\text{EtO})_3$ coordinated with the $\text{C}=\text{O}$ and EO segments in PEGDA, which weakened the restriction of polymer chain segments on Li^+ . Meanwhile, the dense interface formed between $\text{Al}(\text{EtO})_3$ and PEGDA served as the primary Li^+ transport pathway. The liquid components (plasticizer) were confined within the polymer network,

providing high ionic conductivity. The room-temperature ionic conductivity of this CGPE reached $1.05 \times 10^{-3} \text{ S cm}^{-1}$, significantly higher than that of traditional common CPE systems.

To gain a clearer understanding of the relative advantages and disadvantages of four common polymer-based electrolytes, we have highlighted the significant differences among them in key performance metrics, based on a comprehensive review of extensive literature data (Fig. 5). After providing a general introduction to the four common type of polymer-based electrolytes, it is noteworthy that these polymer-based electrolytes predominantly exhibit solid-like macroscopic forms and are extensively applied in solid-state batteries. They also constitute the focal point of this paper. In summary, coordination interaction serves as a central theme that permeates the design and performance optimization of various polymer-based electrolytes. The evolution from single-phase coordination to multi-phase and multi-dimensional synergistic coordination has profoundly influenced ion transport mechanisms, thereby illuminating the future research direction. Specifically, it entails the precise engineering of molecular and interfacial structures to construct novel electrolyte systems with moderate coordination strength and dynamic characteristics, ultimately propelling a significant leap in the performance of solid-state batteries.

3. Coordination chemistry blueprint and fundamentals

Coordination compounds, also known as complexes or coordination complexes, are compounds formed by the central metal atoms or ions bonded to surrounding ligands through coordinate covalent bonds.

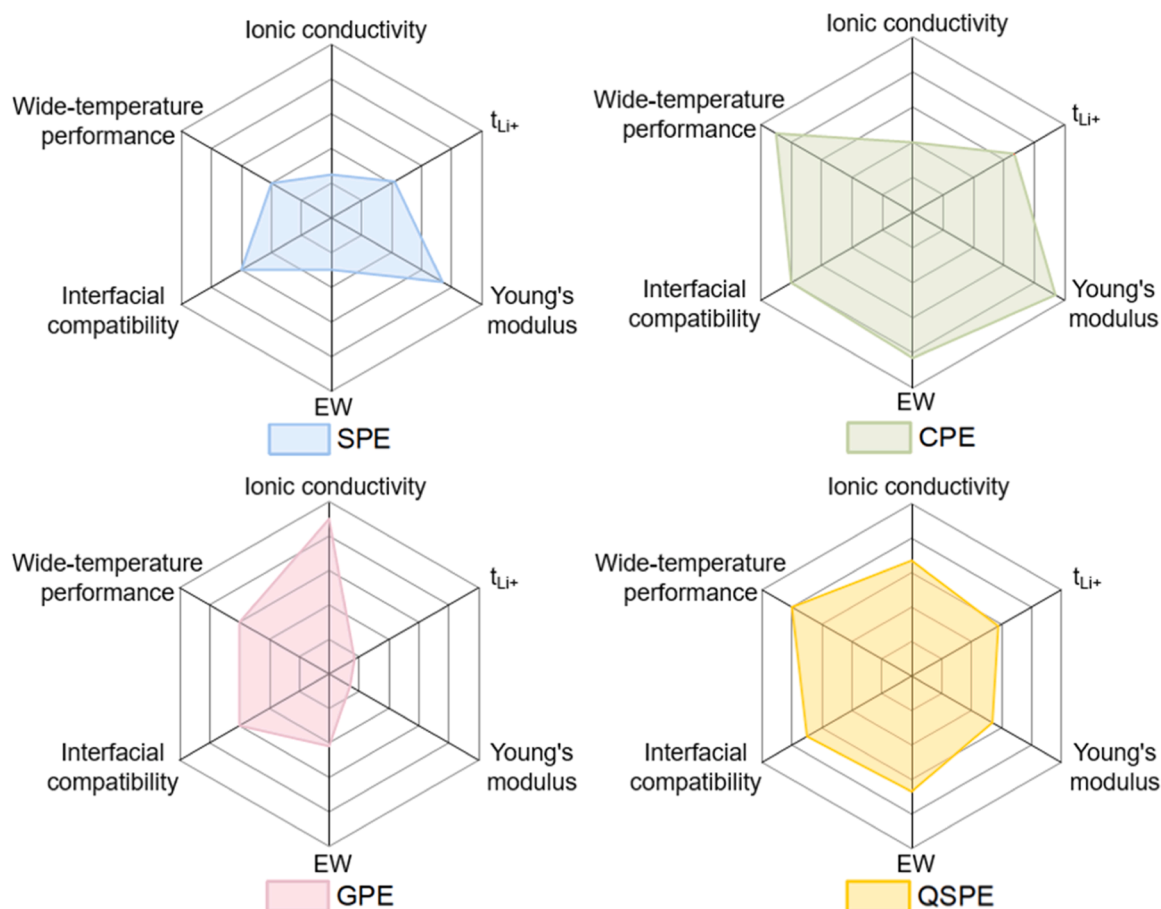


Fig. 5. Radar chart comparing the performance of four polymer-based electrolytes. **Caption:** Data compiled from multiple original studies published between 2020 and 2025, reflecting the performance priorities of different polymer-based electrolytes. This comparison deliberately focuses on typical operating conditions rather than extreme optimal values, as such extremes often rely on ultrathin electrodes, low active material loadings, elevated temperatures, or prohibitively high costs—factors that hinder practical implementation in commercial batteries.

These compounds hold significant importance in chemistry, with their origins traceable to Alfred Werner's coordination theory [65,66]. In 1893, he proposed that metals in coordination compounds possess primary valence and secondary valence, where the former corresponds to the oxidation state and the latter to the coordination number. Coordination compounds can be classified in various ways, primarily based on dimensions such as structure, ligand properties, charge, and stability. These classifications not only facilitate an understanding of the physicochemical properties of the compounds but also find extensive applications in catalysis, pharmaceuticals, and materials science. As evidenced by the polymer-based electrolytes introduced earlier, a deeper comprehension and application of coordination mechanisms contribute significantly to the design of polymer-based electrolytes with superior electrochemical performance. The typical development history of polymer-based electrolytes and the application of coordination mechanisms is illustrated in Fig. 6.

The following sections will focus on the utilization of coordination interactions and characterization techniques in polymer-based electrolytes for solid-state batteries, along with a classification of relevant systems. Additionally, design principles for coordination in various polymer-based electrolytes will be proposed to establish a theoretical foundation for understanding coordination mechanisms. It should be noted that these classifications or design principles are not absolute. Some coordination compounds may belong to multiple categories simultaneously, and their actual structures may be distorted due to electronic effects, such as crystal field theory or ligand field theory.

3.1. Quantifying the coordination landscape

Both ionic conductivity and t_{Li^+} serve as crucial performance indicators for electrolytes, with the Li^+ transport mechanism being directly correlated to coordination strength. It can be said that a profound understanding and precise regulation of coordination strength represent a pivotal step in advancing solid-state battery technology from the laboratory to industrial application. Coordination strength can be evaluated from two perspectives: first, the ion-dipole interactions between cations and ligands, which primarily depend on the inherent properties of the coordinating functional groups and the polymer structure; [67] second, the number of groups coordinated to a single cation, known as the coordination number (CN). For any given ion, its CN is not fixed, as the coordination environment is dynamic [68]. However, CN can be represented by the average number of ligands coordinated to the ion within the system. Considering these two aspects, more precise characterization techniques are required to obtain accurate

coordination strength data, thereby comprehensively elucidating the influence mechanism of coordination chemistry on the ion transport properties of polymer-based electrolytes.

The Anderson team proposed three methods based on conventional nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) measurements for evaluating ionic coordination strength [69]. Among these, two are qualitative approaches. The first is NMR titration, which involves measuring the variation in the chemical shift (δ) of cations (e.g., ^7Li , ^{23}Na) as the polymer concentration increases, thereby reflecting the trend of cation transition from solvent coordination to polymer coordination. The FTIR titration method, on the other hand, is applicable to any cation. It detects the changes in the group such as $\text{C}\equiv\text{N}$ stretching vibration peak ($\sim 2250\text{ cm}^{-1}$) of solvents (e.g., acetonitrile (ACN), propionitrile (PPN)) upon the addition of polymers, specifically monitoring the molecular bond vibrations in ligands sensitive to ionic coordination. After coordination, the $\text{C}\equiv\text{N}$ peak undergoes either a blueshift or a redshift, with the coordination state reflected through variations in peak area. In this regard, by calculating the infrared peak area via deconvolution, a simple formula can be employed to compute the CN value: [70,71]

$$\frac{A_{\text{C-S}}}{A_{\text{C-S}} + A_{\text{F-S}}} = N \frac{C_{\text{Li}}}{C_{\text{S}}} \quad (1)$$

In the formula, $A_{\text{C-S}}$ and $A_{\text{F-S}}$ represent the infrared peak areas of the coordinated solvents and the uncoordinated solvents respectively. C_{Li} and C_{S} represent the concentrations of the lithium salts and the solvents respectively. N represents the average CN of the solvents. However, the limitation of the FTIR titration method lies in the fact that the calculated CN value may not be accurate due to variations in the extinction coefficient, and it is only suitable for relative comparisons. Meanwhile, the aforementioned two qualitative methods are also not applicable to solvent-free systems. Therefore, it is necessary to use a quantitative method capable of analyzing solvent-free systems for more accurate analysis. The quantitative method proposed by the Anderson team can be understood as a measurement of "dissociation energy," addressing the question: How much energy is required to separate an anion and a cation? This energy directly reflects the coordination strength between the polymer and the cation—the stronger the coordination, the more effectively the polymer can pull the ions apart from the "ion pair," and the lower the energy required to break them apart. Then we should know that in a pure polymer (solvent-free), there exists an equilibrium for salt dissolution:

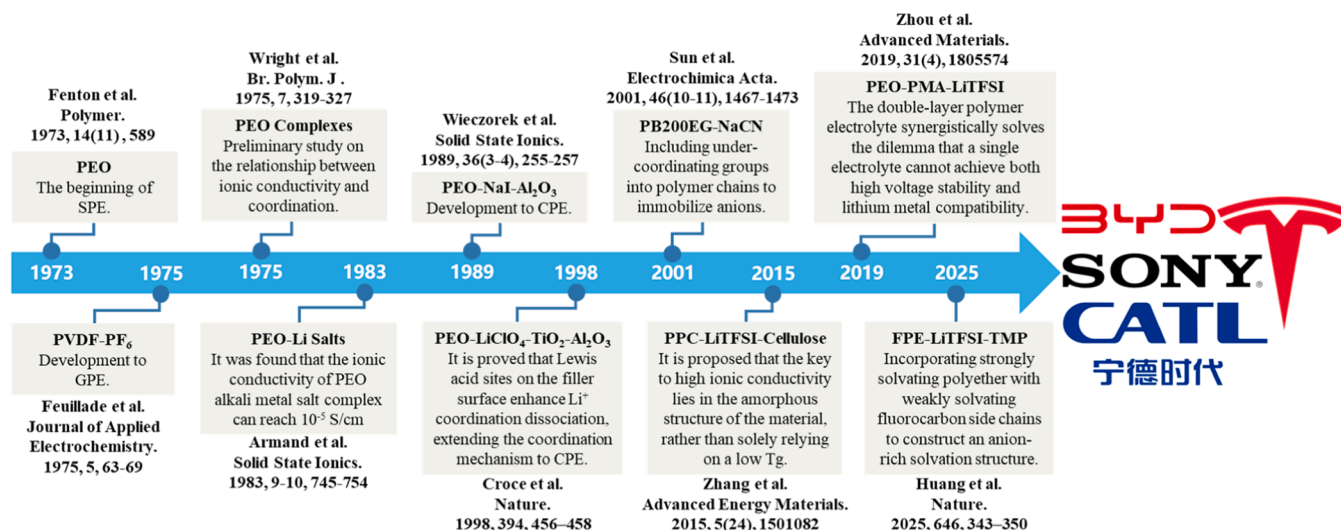


Fig. 6. The typical development history of polymer-based electrolytes and the application of coordination mechanisms.



Here, MX represents associated pairs, while M^+ and X^- denote the dissociated ions that have been successfully solvated by the polymer. The equilibrium constant (K) for this equilibrium is given by:

$$K = \frac{[\text{M}^+][\text{X}^-]}{[\text{MX}]} \quad (3)$$

A larger K value indicates that the equilibrium shifts further to the right, resulting in more free ions in the system. This implies a stronger ability of the polymer to dissociate the salt, i.e., the higher coordination strength. According to this formula, K can be measured by using FTIR. Taking the lithium salt LiTFSI as an example, the TFSI[−] anion has a vibration peak highly sensitive to the coordination environment—the S–N stretching vibration ($\sim 740 \text{ cm}^{-1}$). When ion pairs are formed, the S–N peak of TFSI[−] (in contact with cations) shifts (e.g., to $\sim 748 \text{ cm}^{-1}$). Through deconvolution of the FTIR spectrum, the areas of the two peaks at $\sim 740 \text{ cm}^{-1}$ and $\sim 748 \text{ cm}^{-1}$ can be fitted. The ratio of the areas of these two peaks gives the value of K . By repeating these steps at different temperatures, a series of K values at various temperatures can be obtained. Then, the Van't Hoff equation is introduced: [72]

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4)$$

In the formula, ΔH° represents the standard enthalpy change of the dissociation process, while ΔS° denotes the standard entropy change of the same process. R is the ideal gas constant, and T is the absolute temperature. Plotting $\ln K$ on the vertical axis against $1/T$ on the horizontal axis yields a straight line, where the slope corresponds to $-\Delta H^\circ/R$ and the intercept corresponds to $\Delta S^\circ/R$. According to this, the Gibbs free energy change ΔG° at a specific temperature can be easily calculated:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

A more negative ΔG° indicates that the dissociation reaction proceeds more readily in a spontaneous manner, signifying that the polymer is more effective at withdrawing cations and thus exhibits stronger coordination strength. Conversely, a more positive ΔG° suggests the opposite. Through this approach, the ionic coordination strength can be precisely and quantitatively calculated, facilitating the fine-tuning of an ideal coordination environment. In addition to the three above methods, numerous other techniques offer information from diverse perspectives (structural, kinetic, and energetic). Raman spectroscopy (RS) enables the measurement of energy changes in photons resulting from inelastic scattering during molecular vibrations. Through quantitative or semi-quantitative analysis of peak shifts, peak shape alterations, and peak area ratios, RS complements FTIR measurements [73,74]. Molecular dynamics (MD) simulations can yield the radial distribution function (RDF), calculate the occurrence probability of specific atoms (e.g., EO and C = O) around cations. The integrated area under the first peak of the RDF corresponds to the average coordination number. Additionally, MD simulations can analyze the proportions of solvent-separated ion pairs (SSIP), contact ion pairs (CIP), and aggregates (AGG) within the solvation structure. Based on these proportions, the coordination strength can be inferred (where strong coordination tends to favor the formation of CIP or AGG, while weak coordination leans towards SSIP) [75,76]. X-ray absorption spectroscopy (XAS) is a technique that investigates the local atomic and electronic structures of specific elements within a material by measuring the variation in the material's X-ray absorption coefficient as a function of photon energy [77,78]. XAS spectra are typically divided into two regions: X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The spectral shape in the XANES region is highly sensitive to the geometric arrangement of the central atom and its surrounding coordinating atoms. For instance, significant differences can be observed in the XANES spectra of tetrahedral and octahedral coordination geometries, enabling rapid determination of the chemical

environment and geometric coordination structure. On the other hand, EXAFS can directly provide information on the types of coordinating atoms, coordination distances, coordination numbers, and other factors that directly determine coordination strength. However, XAS measurements typically require a synchrotron radiation source, posing a relatively high experimental threshold. As illustrated in Fig. 7, there are also numerous other characterization methods capable of qualitatively or quantitatively testing coordination strength, such as two-dimensional infrared (2D-IR) dielectric spectroscopy [79], dielectric Relaxation spectroscopy (DRS) [80], X-ray photoelectron spectroscopy (XPS) [81], differential scanning calorimetry (DSC) [82], and so on. More detailed descriptions of these methods will not be elaborated upon here.

In addition to the CN and apparent dissociation thermodynamic parameters (e.g., ΔG°), the binding energy between Li^+ and functional groups offers a more intuitive, molecular-level characterization of coordination strength. While the CN reflects structural features of coordination, ΔG° describes the equilibrium between coordinated and free states; binding energy, by contrast, reveals the fundamental nature of Li^+ –functional group interactions from an energetic perspective. Density functional theory (DFT) calculations are widely employed to estimate such binding energies, thereby offering deep molecular-level insights into the interactions between Li^+ and functional groups [83,84]. It is important to emphasize that, owing to the inherent dynamic nature and varying coordination environments in polymer-based electrolytes, the binding energy of Li^+ with the same functional group may differ across distinct polymer-based electrolyte systems. All the aforementioned characterization techniques have inherent limitations; no single technique can comprehensively, reliably, and quantitatively characterize coordination strength. Therefore, cross-validation—integrating spectroscopic techniques (e.g., FTIR, NMR) with computational simulations (e.g., MD, DFT)—is essential to enhance the reliability of coordination analysis. Meanwhile, by combining the aforementioned multiple characterization techniques to complement each other, a more comprehensive understanding of the coordination environment can be established, which holds significant importance for comprehending the principles of coordination design.

3.2. Coordination number

The previous section has introduced the characterization methods for measuring the CN. Then, how can high-performance polymer-based electrolytes be obtained by regulating CN? In the SPE prepared by Tian et al., the CN between Li^+ and the C = O in 4-acryloylmorpholine (ACMO) was controlled by adjusting the molar ratio of the monomer ACMO to the LiFSI [85]. Based on the calculations derived from FTIR spectroscopy, it is evident that as the content of LiFSI increases, the CN gradually decreases. When the CN is relatively high (>3), Li^+ acts as a cross-linking agent, resulting in high mechanical strength but poor ionic conductivity. Conversely, when the CN is approximately 3, the electrolyte simultaneously exhibits higher room-temperature ionic conductivity ($5.7 \times 10^{-5} \text{ S cm}^{-1}$), satisfied mechanical properties (characterized by moderate stress-strain behavior), and the lowest activation energy (E_a). From the perspective of solvation structure, a higher molar ratio (lithium salt: solvent/polymer monomer) leads to the incorporation of more anions into the solvation sheath of Li^+ [71]. This is clearly the desired outcome we aim for, but the cost implications associated with increasing the amount of lithium salt cannot be overlooked. Propylene carbonate (PC), as a common solvent with strong salt-dissociating ability, is widely employed in liquid electrolyte systems. Nevertheless, its co-intercalation effect with graphite anodes restricts the application of PC in LIB [86]. Compared to employing costly strategies such as high-concentration or locally high-concentration electrolytes, Liu et al. chose to add PEO into a LiTFSI-PC solution to fabricate a GPE [87]. MD simulation results reveal that for a 1 M LiTFSI-PC solution, the CN of Li^+ with the O atoms of PC is 4. Even when the lithium salt concentration is increased to 5 M in a LiTFSI-PC solution, the CN of Li^+ with the O atoms

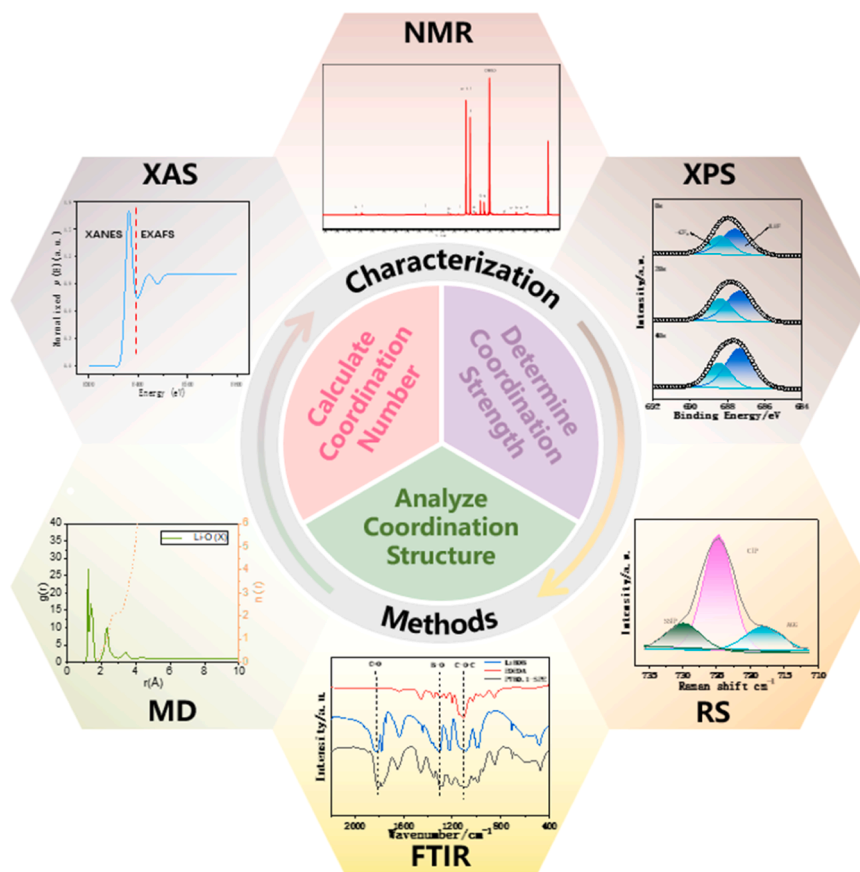


Fig. 7. Advanced characterization methods for coordination strength.

of PC decreases only to 2. Considering the significantly increased cost, this outcome is not satisfactory. However, by introducing PEO into the PC-based electrolyte, PEO competes with PC for coordinating with Li^+ , displacing most of the PC molecules and entering the first solvation sheath of Li^+ . This reduces the coordination number of PC (the CN of Li^+ with the O atoms of PC drops to 1, while the CN with the O atoms of PEO becomes 3), achieving a better effect at a lower cost. Of course, this work does not imply that the influence of PEO on Li^+ transport is always positive. In fact, in a pure PEO-lithium salt polymer combination, Li^+ typically exists in a pentacoordinate structure (4 EO units and 1 anion) [88]. It implies that the strong coordinating effect of PEO will slow down the migration rate of Li^+ . Therefore, for PEO-based systems, it is necessary to introduce other components (additives or fillers) to reduce its CN. Liu et al. prepared a PEO-based CPE by incorporating lignin [89]. Under the influence of an electric field, the -OH groups on lignin form strong intermolecular hydrogen bonds with the EO units on PEO chain segments. In the hydrogen bond ($\text{O}-\text{H}\cdots\text{O}$), the hydrogen atom is electron-deficient and strongly attracts the electron cloud of the EO units, thereby reducing the Lewis basicity of the EO units. Consequently, the CN of Li^+ with EO units decreases from 4 to 3, facilitating its migration. Regardless of which approach, the core of balancing mechanical strength and electrochemical performance lies in the moderate coordination of Li^+ . This is not an isolated parameter but rather a systematic engineering goal achieved through meticulous design of the polymer matrix, selection of lithium salt types, incorporation of nano-fillers, or preparation of copolymers/crosslinked networks to regulate the CN.

Here, it is necessary to provide a more in - depth elaboration on the core design concept of moderate coordination. It should be emphasized that, given the complexity of polymer-based electrolyte systems, a single parameter cannot uniquely define this optimal state. "Moderate" is not a fixed or absolute numerical value or intensity range; rather, it is a

relative concept that depends on the specific system and application objectives. Its essence lies in seeking the best balance between the two mutually - constraining requirements of promoting salt dissociation and ensuring ion migration. In certain systems, a relatively stronger coordination ability is required. For example, in traditional SPE without plasticizers, especially when the polymer matrix has a low dielectric constant and needs to dissolve lithium salts with high lattice energy, the primary challenge is to achieve effective dissociation of lithium salts. In this case, "moderate" means that the coordination effect must be strong enough to effectively overcome the lattice energy of the lithium salts, pulling Li^+ out of ion pairs or aggregates to form freely - moving charge carriers [90,91]. If the coordination is too weak, the lithium salts cannot dissociate, and ionic conductivity will be out of the question. In other systems that pursue high-rate performance and low interfacial impedance, a relatively weaker coordination ability is "moderate" [92,93]. The desolvation process of Li^+ at the electrode interface becomes the rate controlling step. At this time, if the coordination effect between Li^+ and polymer chains or solvent molecules is too strong, it will lead to an extremely high desolvation energy barrier. Li^+ will be anchored at the coordination sites, making it difficult to rapidly escape from the solvation sheath and deposit onto the negative electrode, thus seriously affecting the fast-charging performance of the battery. More specifically, integrating strong coordination polymer matrices and weak coordination polymer matrices into a single system through ingenious molecular engineering (e.g., blending or copolymerization), allowing them to perform their respective functions—where the strong coordination part is responsible for dissociation and the weak coordination part for migration; or introducing competing cations to neutralize strong coordination; as well as regulating and guiding anions, are all concrete manifestations of moderate coordination [94,95]. The work on these systems will be further elaborated in the following sections.

3.3. Denticity vs. coordination number

Coordination compounds are typically classified based on CN, denticity, geometric configuration, ligand type, coordination sphere charge, number of metal centers, as well as the properties of cations/anions. In the majority of SPE research, the primary focus lies on CN, denticity, and geometric configuration. The various ion transport mechanisms in SPE have been briefly introduced in the preceding text, and the denticity and coordination mode of ligands directly influence the types and efficiency of ion transport, thereby determining the overall performance of the electrolyte. Denticity and CN are two concepts that are easily confused, yet they differ fundamentally in their definitions. CN describes the total number of coordinating atoms directly bonded to a central ion, which can originate from one or multiple different ligands. In contrast, denticity refers to the number of coordinating atoms that a single ligand molecule (or an independent coordinating unit within a polymer) can provide to the same central ion. Fig. 8 illustrates various coordination types and the distinction between denticity and CN. For instance, a cyanide unit can coordinate with only one central ion at most, making it a typical monodentate ligand. Phenanthroline, with two nitrogen atoms capable of donating lone pairs of electrons as coordinating atoms, is a bidentate ligand. Table 1 lists common monodentate and multidentate ligands. Based on the denticity of ligands, coordination types can be broadly classified into monodentate coordination, multidentate coordination, and chelate coordination.

3.3.1. Dynamic and labile monodentate coordination

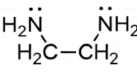
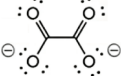
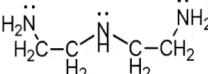
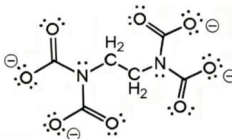
Monodentate coordination refers to a scenario where only one atom within an independent ligand molecule or polymer chain segment is capable of coordinating with a central metal ion. A common example is the monodentate coordination formed between the C = O of EC solvent molecules and Li^+ [96]. In PEO-based polymer electrolyte systems, Li^+ typically coordinates with multiple EO units on the PEO chain segments. However, since each ether oxygen group originates from an independent repeating chain segment unit, this can also be defined as monodentate coordination. Specifically, in ion transport, this manifests as Li^+ sliding along the polymer chain. This is because monodentate coordination bonds are relatively weak with low bond energy, making them prone to breakage and reformation, which facilitates ion hopping transport. Due to the dynamic nature of monodentate coordination bonds, it is often the preferred strategy when pursuing high ionic conductivity. Nevertheless, the inability of monodentate coordination to form stable crosslinked networks is a major drawback, leading to issues such as crystallinity and poor mechanical properties.

3.3.2. Multidentate coordination: the strength-mobility interplay

Multidentate coordination refers to the scenario where a single ligand molecule possesses multiple coordinating atoms that bind to the same central metal ion. These coordinating atoms do not necessarily form a cyclic structure, or if they do, the ring may be unstable. For example, ethylenediamine (en) is a typical bidentate ligand with two nitrogen atoms that can simultaneously coordinate with the same central metal ion [97]. The combined action of multiple coordinating atoms

Table 1

Different types of common ligands.

Ligand	Dentate	Name
F^-	mono	Fluoride ion
Cl^-	mono	Chloride ion
Br^-	mono	Bromide ion
CN^-	mono	Cyanide ion
SCN^-	mono (via S)	Thiocyanate ion
NCS^-	mono (via N)	Isothiocyanate ion
FSI^-	mono	Bis(fluorosulfonyl)imide ion
PF_6^-	mono	Hexafluorophosphate ion
$-\text{SO}_3^-$	mono	Sulfonate ion
$\text{C}=\text{O}$	mono	Carbonyl
$-\text{O}-$	mono	Ether oxygen
$-\text{OH}$	mono	Hydroxyl
$-\text{CN}$	mono	Nitrile
EC	mono (via C = O)	Ethylene Carbonate
TFSI^-	mono/bi	Bis(trifluoromethanesulfonyl)imide ion
DME	bi (via two -O-)	1,2-Dimethoxyethane
	bi	Ethylenediamine (en)
	bi	Oxalate ion ($\text{C}_2\text{O}_4^{2-}$)
	tri	Diethylenetriamine(dien)
	hexa	Ethylenediaminetetraacetic acid (EDTA)

far surpasses that of monodentate coordination in terms of solvating cations, effectively promoting salt dissociation and increasing the concentration of free ions. Simultaneously, a single Li^+ ion can serve as the "crosslinking point" between multiple polymer chains, forming a physical crosslinked network. This significantly enhances the mechanical strength of the electrolyte and effectively suppresses lithium dendrite penetration, which is one of the most core functions of multidentate coordination. Due to the "anchoring" of anions on polymer chains or their binding with fillers, while Li^+ remains the primary mobile ion, multidentate coordination facilitates the preparation of electrolytes with high t_{Li^+} . However, the strong coordinating interactions and the formation of crosslinked networks may restrict the movement of polymer chain segments, increasing the energy barrier for ion hopping and, to a certain extent, suppressing the ion migration rate. Wang et al. introduced CsPF_6 to partially replace LiTFSI and added a small amount of 2,4,6-trifluoroaniline (2,4,6-TFA) into the base PEO-PVDF + LLZTO + LiTFSI CPE system, creating a complex coordination environment [98]. In this system, 2,4,6-TFA competes with TFSI^- for coordinating with Li^+ . The coordination interaction between 2,4,6-TFA and Li^+ is relatively weak (compared to the strong electrostatic interaction between TFSI^- and Li^+), which weakens the coordination environment around Li^+ . Meanwhile, TFSI^- forms a bidentate coordination structure with both Li^+ and Cs^+ . Cs^+ competes with Li^+ for the coordination sites on TFSI^- , thereby reducing the interaction between TFSI^- and Li^+ and releasing more free Li^+ . After modification, the ionic conductivity of the CPE reaches $6.25 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, which is more than twice that of the original base CPE. Simultaneously, the t_{Li^+} increases from 0.27 to 0.61. This work shows a unique understanding of the

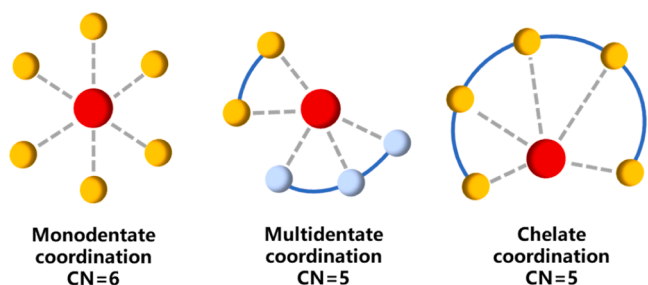


Fig. 8. Schematic of coordination types classified by ligand denticity.

application of multidentate coordination.

3.3.3. Chelate coordination: precision control and ring

Chelate coordination represents a specialized form of multidentate coordination, wherein a single ligand utilizes two or more coordinating atoms to bind with the same central metal ion, forming one or more thermodynamically stable five- or six-membered ring structures. This "ring-forming" effect is known as the chelate effect, which imparts significant stability to the complex. For example, the molecular structure of ethylenediaminetetraacetic acid (EDTA) contains six potential coordination atoms: two -NH_3 and four $\text{C}=\text{O}$, often forming hexadentate chelates with divalent transition metal ions [99]. Another notable example is the coordination of Li^+ with three EO units on diglyme (G2), which forms a five-membered ring structure. The chelate effect in this case renders the complex highly stable [100]. Xie et al. synthesized a series of fluorinated linear polyesters by alternately incorporating diester units, linear diol units, and fluorinated end-capping groups [101]. According to the chemical shifts observed in ^7Li NMR spectroscopy, it was determined that the fluorinated linear polyester exhibiting the strongest coordination interaction with Li^+ formed a six-membered ring chelate coordination structure, whereas those with relatively weaker coordination interactions formed five-membered coordination rings. This discovery confirms that the coordination mode is a critical factor influencing the strength of Li^+ -ligand interactions. In another related study by the same team, polycarbonate electrolytes (PCE), polyoxalate electrolytes (POE), and polymalonate electrolytes (PME) were synthesized via straightforward ester exchange reactions [102]. Notably, both oxalate and malonate units contain two $\text{C}=\text{O}$ per repeating unit, enabling the formation of five- or six-membered cyclic chelate structures with Li^+ . In contrast, the $\text{C}=\text{O}$ group can only form non-chelate coordination with Li^+ through a single carbonyl oxygen. DFT calculations of binding energies revealed that chelate coordination results in stronger interactions with Li^+ , facilitating lithium salt dissociation while enhancing oxidative stability.

In general terms, chelate coordination can be seen as an advanced version of multidentate coordination. While it excels in salt dissociation capability and mechanical properties, it also tends to "lock" ions within the cyclic structure, resulting in low ionic conductivity. Given these extreme advantages and disadvantages, the key aspect is to prevent the formation of continuous, high density chelation sites within the system. A common strategy is to sparsely distribute chelate units as crosslinking points within a flexible polymer matrix that provides ion transport pathways. Considering that each type of coordination has its own advantages and disadvantages, the future development direction should involve the application of molecular engineering to ingeniously integrate dynamic monodentate coordination and stable multidentate coordination within a single material. This approach aims to fabricate the next-generation polymer-based electrolytes that simultaneously possess high ionic conductivity, high safety, and long cycle life.

3.4. From coordination parameters to battery performance: establishing the causal link

Through the systematic characterization and classification of coordination strength, CN, and coordination mode, we have gained a deeper understanding of the physicochemical nature of ion transport in polymer-based electrolytes at the microscopic level. These theoretical foundations provide a basis for analyzing the performance bottlenecks of existing electrolyte systems. Although these single coordination descriptors can offer valuable insights into the local ionic environment, the actual battery performance ultimately depends on the synergistic interplay of multiple parameters. Therefore, establishing a causal relationship between the molecular-scale coordination environment and macroscopic electrochemical performance is imperative for the rational design of polymer-based electrolytes.

From the perspective of bulk transport, the migration of Li^+ in

polymer-based electrolytes typically involves two coupled processes: local coordination site exchange and long-range transport assisted by the motion of polymer chain segments. The coordination strength between Li^+ and ligands, along with the average CN, are two crucial factors determining the migratory capability of Li^+ . On one hand, sufficiently strong coordination strength is essential for overcoming the lattice energy of lithium salts and promoting the dissociation of Li^+ into free charge carriers, which serves as the foundation for all ionic conduction. However, excessively strong coordination creates deep potential wells, resulting in a prohibitively high E_a required for Li^+ to detach from coordination sites. This kinetically traps Li^+ in place, impeding its migration. This trade-off directly constrains ionic conductivity and rate performance. Similarly, an excessively high CN may create a deeply trapping environment that hinders dynamic ion exchange, while an excessively low CN leads to incomplete salt dissociation and severe ion association. Therefore, a moderate coordination environment must simultaneously satisfy two requirements: (i) sufficiently strong local interactions to enable effective dissociation of lithium salts and stabilize ionic conduction pathways; and (ii) sufficiently dynamic ligand exchange capabilities to minimize the energy barrier for Li^+ hopping and facilitate rapid ion redistribution under practical current densities. On the other hand, the coordination bonds formed between Li^+ and polar functional groups on polymer chains can act as transient physical crosslinking points. Higher coordination strength increases the density and lifetime of these crosslinking points, thereby restricting the mobility of polymer chains, elevating the T_g , and ultimately suppressing Li^+ transport. Based on the above considerations, strategies to weaken Li^+ -polymer interactions—such as introducing competitive ligands (e.g., plasticizers, other cations) or employing polymers with inherently moderate coordination capabilities (e.g., polyesters, polycarbonates)—can effectively free polymer chains, enhance segmental motion, and facilitate local coordination site exchange of Li^+ , thereby significantly improving ionic conductivity.

While optimizing ionic conductivity, it is also imperative to address anions that contribute to the overall ionic conductivity but do not participate in the battery current, thereby inducing concentration polarization. Coordination chemistry also offers potent regulatory tools for this purpose. By designing polymer backbones or additives containing Lewis acidic sites (e.g., boron-containing groups, unsaturated metal centers in fillers) or positively charged groups (e.g., quaternary ammonium salts, imidazolium cations), anions acting as Lewis bases can be selectively coordinated or "trapped." This targeted coordination significantly reduces the mobility of anions, thereby enhancing the t_{Li^+} . Consequently, the salt concentration gradients during charge-discharge cycles are effectively mitigated, which is crucial for suppressing lithium dendrite growth, enabling high-rate operation, and achieving excellent cycling stability.

At the electrode/electrolyte interface, coordination chemistry further governs the interfacial reaction pathways and deposition behaviors. The composition of the first solvation shell of Li^+ is determined by competitive coordination among polymer chain segments, solvent molecules, anions, and additives, which fundamentally regulates the interfacial reaction behaviors at the electrode surface. For instance, a weakly solvating environment forces more anions into the first solvation shell of Li^+ . When this coordination structure undergoes reduction at the anode surface, the anion-derived solvation shell decomposes, generating a predominantly inorganic, structurally stable solid electrolyte interphase (SEI). A dense and uniform SEI plays a decisive role in physically blocking lithium dendrites, preventing continuous electrolyte decomposition, and ensuring uniform distribution of Li^+ . This directly manifests as enhanced Coulombic efficiency, prolonged cycle life, and improved battery safety.

Notably, these coordination descriptors inherently exhibit intricate coupling relationships. For instance, increasing the density of electron-donating groups in polymers may enhance salt dissociation but could simultaneously exacerbate Li^+ trapping. Similarly, the introduction of

fillers, while suppressing crystallization and reconstructing transport pathways, may also alter local ion aggregation behaviors. Therefore, future design of polymer-based electrolytes should not focus solely on optimizing individual descriptors in isolation but rather on the coupling relationships among them, as well as the dynamic equilibrium among salt dissociation, Li^+ transport kinetics, anion regulation, and interfacial stability. To this end, Table 2 summarizes the key semi-quantitative coordination descriptors governing the performance of polymer-based electrolytes. This descriptor-based framework provides a practical roadmap for the engineering development of future polymer-based electrolytes. Building upon this foundation, we will further explore the specific applications of coordination chemistry in various polymer-based electrolytes and provide a detailed analysis of advanced coordination strategies developed in recent years: starting from the classic PEO system and progressively extending to multicomponent synergistic coordination strategies, elucidating how precise coordination engineering can achieve the synergistic enhancement of ionic conductivity, t_{Li^+} , interfacial stability and practical battery performance.

4. Recent development of coordination engineering in polymer-based electrolytes

The central atom, positioned at the geometric center of the inner coordination sphere in a coordination compound, is the core of the coordination ions. Typically, central atoms are positively charged metal ions with vacant orbitals. For lithium-based batteries, the ionic conductivity and the t_{Li^+} are of particular concern, as these factors significantly determine battery performance [103]. Therefore, the mechanism by which ions are more effectively transported within polymer-based electrolytes has become a focal point of research. It is widely recognized that in conventional polymer-based electrolytes, Li^+ are primarily transported through the segmental motion of the polymer main chains [104]. Due to the coordination between cations and the functional groups on polymers, their transport is closely related to the local motion of polymer chains. PEO, as a commonly used polymer host material, exhibits good lithium salt solubility. It has been extensively studied because its polymer chain contains EO units that serve as Li^+ -coordinating moieties [105–108]. In addition to PEO, polymers such as polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), polyurethane (PU), and polyvinylpyrrolidone (PVP) are also employed as host materials for preparing polymer-based electrolytes. Different polymer hosts possess distinct functional groups, which imply varied coordination environments. So it is of paramount importance to deepen the understanding of the coordination interactions between Li^+ and various functional groups.

The coordination interaction between the EO units on PEO segments

and Li^+ forms the basis of the classic ion transport mechanism. However, with the escalating demands for improved electrochemical performance, the inherent limitations of the PEO system have gradually become apparent. Its high crystallinity restricts continuous pathways for Li^+ transfer, resulting in unsatisfactory ionic conductivity. Moreover, the excessively strong coordination between EO units and Li^+ fixes the Li^+ , thereby limiting their mobility and leading to a considerably low t_{Li^+} ($\approx 0.2\text{--}0.3$) in PEO-based electrolytes [109–111]. Based on this, scientists turned their attention to polyester and polycarbonate polymers for application in solid-state batteries [112–115]. Because compared to EO units, the $\text{C}=\text{O}$ groups exhibit significantly weaker coordination strength with Li^+ , thereby enabling a higher t_{Li^+} [104,116]. For example, poly(ϵ -caprolactone) and poly(trimethylene carbonate) have been widely studied [117–119]. However, polyester and polycarbonate also suffer from issues such as high crystallinity at room-temperature and narrow electrochemical window (EW), which are detrimental to the formation of a uniform and stable SEI [120]. Reducing the coordination strength between functional groups and Li^+ essentially involves decreasing the electron density of the O atoms on EO units. Drawing on this concept, poly(tetrahydrofuran) (PTHF) was considered. Its structure is similar to that of PEO, but it contains fewer heteroatomic oxygens in the main chain, thereby weakening the Li^+ -O interaction and facilitating easier dissociation of Li^+ compared to PEO [121]. Similarly, aliphatic ketone-based polymer-based electrolytes exhibit weak coordination between their ketone carbonyl groups and Li^+ , which promotes Li^+ conduction [122–124]. In addition, strategies such as incorporating additives into PEO-based polymers [125,126], modifying PEO polymer segments [50,127,128], designing functional groups [129,130], introducing side chains [131], and fluorination have also been explored [132]. Table 3 presents some key data for typical and recently developed polymer-based electrolytes, including structural descriptions, t_{Li^+} , ionic conductivity, and EW. Compared to conventional PEO-based electrolytes, these polymer-based electrolytes exhibit reduced crystallinity and weaker Li^+ -O interactions, leading to significantly enhanced ionic conductivity and t_{Li^+} . This progress provides extensive strategies for improving the performance of polymer-based electrolytes.

4.1. Recent development of polymer-based electrolytes focuses on lithium ion coordination

To achieve more rational coordination between Li^+ and functional groups on various polymers, scientists have made numerous improvements by focusing on regulating Li^+ coordination. Given that the electrochemical performance of polymer-based electrolytes is closely tied to their solvation structure, strategically optimizing the solvation structure through the modulation of coordination strength between polymer

Table 2

Semi-quantitative coordination descriptors and practical design guidelines for polymer-based electrolytes.

Coordination descriptor	Insufficient coordination	Moderate coordination	Excessive coordination	Electrochemical implications / design guidance
Li^+ -ligand coordination strength Average CN	Insufficient salt dissociation; poor ion availability Incomplete Li^+ solvation; unstable transport pathways	Moderate binding enables both salt dissociation and fast Li^+ exchange Dynamic and continuous Li^+ transport	Li^+ trapping; slow segmental exchange and sluggish hopping Dense solvation shells and high transport resistance	A balanced interaction strength is critical to simultaneously ensure high ionic conductivity and low E_a Optimizing CN can reduce migration barriers while maintaining structural continuity
Competitive cation coordination	Unable to achieve competitive coordination	Reconstructed solvation shell, reduced crystallinity, and improved Li^+ transport	Disrupt structural integrity and reduce Li^+ transport selectivity	Competitive coordination should be tailored to optimize solvation structure and decouple ion transport from polymer chains
Anion coordination	Poor anion participation may lead to unstable interfaces	Moderate anion-derived solvation can improve interface stability	Excessive ion aggregation reduces free Li^+ concentration and increases polarization	Controlled anion coordination helps construct robust SEI/CEI while minimizing polarization
Filler / additive coordination	Insufficient interfacial interaction yields poor dispersion	Moderate Lewis acid/base interactions create fast transport pathways	Excessive Li^+ immobilization or rigidification of polymer matrix	Functional fillers should regulate local coordination rather than simply increase rigidity

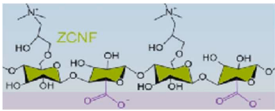
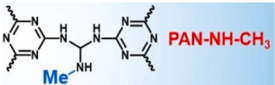
Table 3

Key data for typical and recently developed polymer-based electrolytes.

Type	Main materials	Structural formula	t_{Li}^+	Ionic conductivity [$S\ cm^{-1}$] at room temperature	EW [V]	T_g [$^{\circ}C$]	Refs.
SPE	PEO		0.2	10^{-6}	3.9	-64	[34]
SPE	PM(BMA)S		0.72	2.6×10^{-5}	4.8	-76	[118]
SPE	xPTHF10		0.53	1.2×10^{-4}	4.8	-65.7	[121]
SPE	PEGDA+ AAA+ DAAM		0.87	3.6×10^{-5}	4.95	-36.9	[122]
SPE	PEO+IPDI		0.61	3×10^{-3}	5	—	[133]
SPE	PEGMA+ EOEOEA+ EC		0.78	2.97×10^{-4}	4.8	-52.5	[50]
SPE	HFMA+ HFBA+ IL		0.79	1.59×10^{-3}	4.8	-42	[134]
GPE	PEO+ PVDF-HFP		—	8.1×10^{-4}	4.3	-42.1	[135]
SPE	LiCTFPB+ TTEG		0.92	3.53×10^{-4}	4.8	-69	[136]
SPE	PIM-CONH ₂		0.88	1.08×10^{-3}	5.2	22	[137]
CPE	DOL+ KH560@InF ₃		0.71	2.1×10^{-4}	4.1	—	[138]
SPE	PEGDA+ AAA		0.37	1.1×10^{-4}	4.8	46.5	[123]

(continued on next page)

Table 3 (continued)

Type	Main materials	Structural formula	t_{Li^+}	Ionic conductivity [S cm^{-1}] at room temperature	EW [V]	T_g [$^{\circ}\text{C}$]	Refs.
SPE	PEO+ZCNF		0.62	5.37×10^{-4} (60 $^{\circ}\text{C}$)	4.51	-38	[139]
CPE	PEO+ PAN-NH-CH ₃		0.39	6.92×10^{-5}	4.8	-52.3	[140]
CPE	PEO+ Br-TPC+ TAPB		0.53	6.21×10^{-5}	5.15	-55.4	[141]

chains and Li^+ represents a highly effective approach [142,143].

4.1.1. Modulating solvation structure through coordination

In electrolytes, both solvent molecules and anions can act as ligands, coordinating with Li^+ through ion-dipole or ion-ion interactions. The competitive coordination determines the solvation structure of Li^+ . Furthermore, the composition and dynamic characteristics of the solvation shell significantly influence the electrochemical performance of a battery [144–146]. However, traditional solvation structures typically involve strong solvent- Li^+ interactions, which may result in high desolvation energy barriers, thereby limiting the fast-charging capability and low-temperature performance of batteries. Based on this, researchers have proposed the concept of weakly solvating structure by optimizing solvent or electrolyte formulations (e.g., choosing solvents with low dielectric constants and poor solvating ability) to reduce the binding strength between Li^+ and solvent molecules, aiming to achieve superior electrochemical performance [147–149]. As the content of

solvent molecules decreases, more lithium salt anions are incorporated into the Li^+ solvation sheath. This facilitates a reduction in the desolvation energy and leads to the formation of a more uniform and dense SEI layer, this point will be discussed further below [150]. Consequently, even with moderate to low lithium salt concentrations, high-quality solvation structures rich in CIP and AGG can be achieved. Considering the respective advantages and disadvantages of polyether and polyesters, as well as the potential drawback of uneven Li^+ deposition due to the lack of anion participation in the solvation structure, Liu et al. combined the strong Li^+ -O (ether) and weak Li^+ -O (ester) coordination with the steric hindrance effects in polymer-based electrolyte [151]. The synthesized polymer features a main chain with one ether group, two ester groups, and one methyl group acting as steric hindrance (Fig. 9a). This design ultimately resulted in an anion-rich solvation structure, and the t_{Li^+} up to 0.8. The cell assembled with NCM523 cathode material at a high loading of 7.5 mg cm^{-2} exhibits stable cycling for 150 cycles at 0.2C, retaining 73% of its initial capacity.

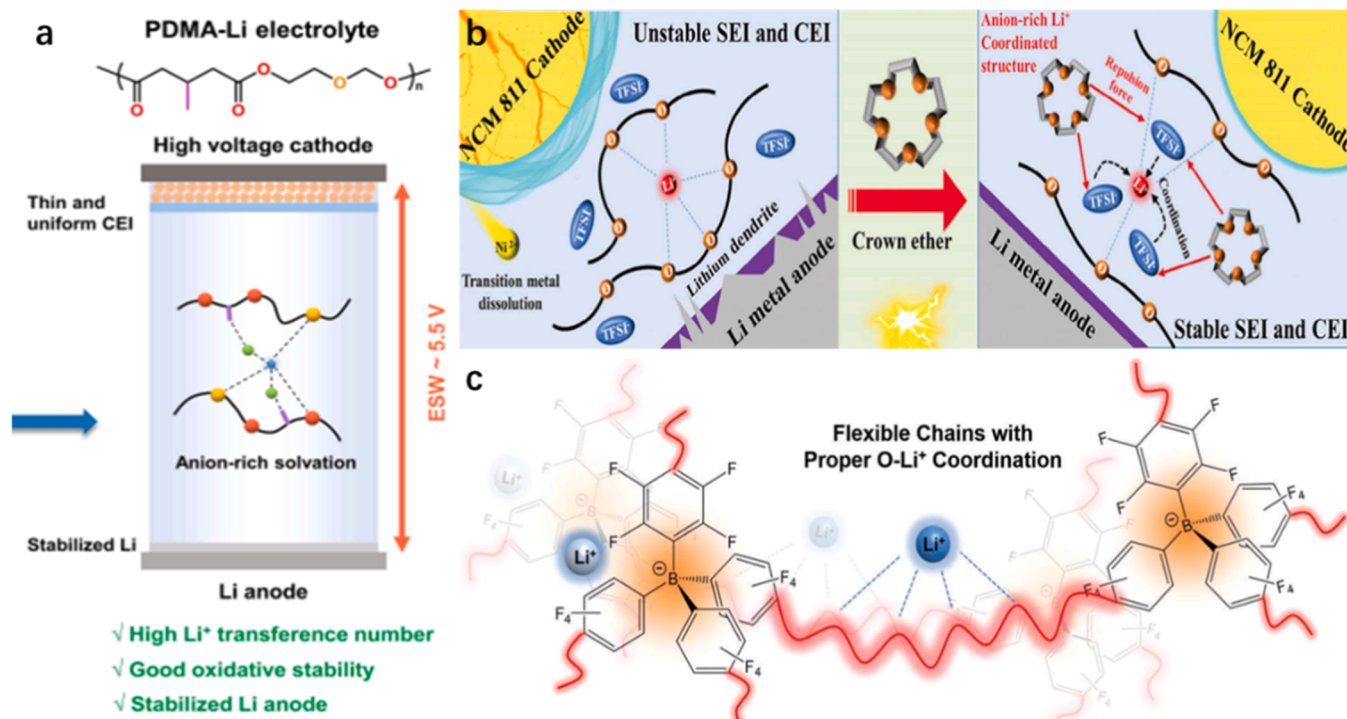


Fig. 9. a) Weakly solvating structure. Reproduced with permission [151]. Copyright 2024, Wiley-VCH. b) Molecule crowding strategy. Reproduced with permission [154]. Copyright 2024, Wiley-VCH. c) The fluorinated phenyl rings disperse the negative charge, thereby reducing the binding energy between the Li^+ and anions. Reproduced with permission [136]. Copyright 2022, Wiley-VCH.

The approach of weakly solvating structure has also been effectively employed by Ye et al. [152] They designed a polycarbonate-based copolymer electrolyte featuring a weak solvation structure for Li^+ , which allows a greater number of anions to be incorporated into the solvation shell. The hybridization of cyclic and linear carbonate segments within the main chain weakens the coordination between Li^+ and $\text{C}=\text{O}$ groups, thereby enhancing Li^+ migration kinetics. This design achieves a notably high t_{Li^+} (0.76 at 25 °C).

Typically, the use of high-polarity solvents and the construction of anion-rich solvation structures are mutually contradictory. However, Wang et al. resolved this issue through a unique approach [153]. By introducing the high-polarity solvent SN into the GPE based on a poly (methyl methacrylate-co-methylacrylamide) copolymer. Due to the stronger coordination capability of SN with Li^+ , it effectively "sequesters" Li^+ that were originally bound to hydrogen-bonding sites on the polymer, while simultaneously preserving the hydrogen-bonding network of the polymer. The ingenuity lies in the fact that the hydrogen-bonding network compresses the available space for solvent molecules and anions, thereby inducing molecular aggregation. The crowding effect resulting from this aggregation "forces" more anions into the solvation shell of Li^+ , achieving a reconciliation between the use of high-polarity solvents and the formation of a weakly solvating structure. This concept of utilizing the molecule crowding strategy to force anions into the Li coordination sheath was previously proposed by the Zhang's team [154]. As illustrated in Fig. 9b, they introduced 15-crown-5 into the SPE, leveraging its electrostatic repulsion against lithium salt anions to achieve an anion-rich coordination structure. This indirectly weakened the coordination between Li^+ and the polymer chains, thereby facilitating Li^+ transport. Despite variations in solvent or additive selection, the fundamental approach involves modulating the coordination strength between polymer chains and Li^+ to optimize the solvation structure. Consequently, the symmetric $\text{Li}||\text{Li}$ cell can stably operate over 4360 h, and the assembled pouch cell shows excellent stability (89.42% capacity retention after 400 cycles).

Although weakly solvating electrolytes exhibit excellent electrochemical stability at the interfaces of high-voltage cathodes and lithium metal anode, the reduction in solvation strength can lead to decreased salt solubility and lower ionic conductivity [130,155,156]. While most of the aforementioned strategies primarily focus on adjusting the types and ratios of solvents with varying solvation strengths to achieve optimal performance, Lian et al. took a different approach to balance the advantages and disadvantages of strong and weak solvation [157]. Although it is not a polymer-based electrolyte, its concept is worthy of reference in the field of polymer-based electrolytes. Specifically, they developed a cyano-substituted cyclic ether, 4-cyanotetrahydropyran (CNTHP), which does not simply enhance or weaken the solvent's coordination ability. Instead, it redesigns the coordination environment by introducing a new coordination site—the nitrogen atom. Compared to conventional tetrahydropyran (THP), where the negative charge is predominantly localized on the O atoms, the additional -CN group in CNTHP shifts the charge density to the nitrogen atoms. The electron-withdrawing effect of the -CN group weakens the coordinating ability of the EO group, while the nitrogen atom provides a new coordination site for Li^+ . The coordination strength of the nitrogen is well-balanced: it is neither too strong like the EO group, which impedes Li^+ transport, nor too weak as in fully weak-solvation electrolytes, which suffer from low Li-salt solubility. This design achieves a non-chelating multidentate ligand with moderate solvation ability. Its linear structure facilitates rapid Li^+ desolvation and migration, thereby enhancing ion transport kinetics.

4.1.2. Precise charge regulation

Dong et al. shifted their focus on the charge-transfer mechanism occurring between adjacent solvent molecules within the Li solvation sheath [158]. Traditionally, charge transfer has been primarily understood to take place at the electrode-electrolyte interface [159].

However, this team pointed out that a flow or redistribution of charge could also occur among solvent molecules inside the solvation sheath. For example, when the EC molecules donate the electron density to Li^+ , it becomes more electron-deficient, potentially affecting neighboring EC molecules. Building on this concept, an amide polymer encapsulation matrix (APEM) was introduced as an artificial electron acceptor, with EC in the electrolyte serving as the electron donor. Since the amide groups ($-\text{CO}-\text{NH}-$) in APEM are electron-deficient, they can attract the π -electrons from the $\text{C}=\text{O}$ groups of EC, effectively "drawing" EC out of the Li solvation sheath. This indirectly promotes cation-anion coordination within the solvation sheath, leading to the formation of AGG and CIP structures. Such an arrangement enhances anion participation in interfacial reactions, offering a novel approach to modulate the solvation structure. A similar charge-regulation strategy was earlier proposed by Li et al. in the design of SPE [136]. As illustrated in Fig. 9c, the $[\text{B}(\text{C}_6\text{F}_4)_4]^-$ anion disperses its negative charge across four fluorinated phenyl rings, reducing the binding energy with Li^+ and facilitating easier Li^+ dissociation. The unique structure diminishes Li^+ -anion interactions and optimizes the O- Li^+ coordination strength (with moderate coordination between four EO units and Li^+). This SPE exhibits a room-temperature ionic conductivity of $3.53 \times 10^{-4} \text{ S cm}^{-1}$, a high t_{Li^+} of 0.92, and a wide EW exceeding 4.8 V. Obviously, in electrochemical systems, charge distribution determines the interaction strength among solvents, anions, polymers, and Li^+ , thereby influencing the coordination environment of Li^+ . Therefore, precise charge regulation can also be regarded as a coordination method.

4.1.3. Stable SEI layer and lithium dendrite suppression

Coordination chemistry not only plays a pivotal role in regulating ion transport in the bulk phase but also exerts a dominant influence on the interfacial processes of polymer-based electrolytes, particularly in the formation of the SEI and the suppression of lithium dendrite growth.

From the perspective of the underlying mechanisms, the coordination environment of Li^+ directly determines its local chemical micro-environment and reduction behavior at the electrode interface. Specifically, the first coordination shell, which is composed of interactions between Li^+ and polymer functional groups and/or anions, governs which components are preferentially reduced during the initial electrochemical reactions. When certain functional groups or anions form strong coordination bonds with Li^+ , they become more prone to participating in interfacial decomposition reactions, thereby facilitating SEI formation [160–162]. Therefore, using coordination chemistry can indirectly regulate the chemical composition (e.g., inorganic-rich or organic-rich types), structural uniformity, and mechanical stability of the SEI layer. Additionally, the coordination strength of Li^+ influences the desolvation kinetics at the interface: overly strong coordination can hinder Li^+ release, increasing interfacial impedance, while insufficient coordination may lead to an unstable SEI, triggering continuous side reactions and dendrite formation.

These mechanistic insights have been extensively validated in recent studies, particularly through strategies that control interfacial chemistry by modulating Li^+ coordination. In conventional polymer-based electrolytes, interfacial reduction reactions are primarily dominated by the polymer matrix or residual solvent molecules, potentially resulting in the formation of an SEI layer rich in organic components with fragile mechanical properties [163,164]. Shen et al. significantly weakened the Li-O coordination interaction within polymer electrolyte by introducing semi-ionic C-F bonds, while simultaneously enhancing the interaction between Li^+ and TFSI $^-$ [132]. Consequently, TFSI $^-$ were able to enter the first solvation sheath of Li^+ and were preferentially reduced at the lithium metal surface, leading to the formation of an inorganic LiF-rich SEI layer. Meanwhile, the dual-layer structure—with an inner layer predominantly composed of inorganic compounds (e.g., LiF, Li_2O) and an outer layer primarily consisting of organic components, effectively suppressed lithium dendrite growth and promoted uniform lithium deposition. As a result, the assembled $\text{Li}||\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ battery

presents outstanding capacity retention and cycling stability (79.1% capacity retention after 500 cycles at 0.5C) at 40 °C. Owing to the high mechanical strength, excellent chemical stability, and low electronic conductivity of LiF, such fluorine-containing interfacial modulation strategies that leverage coordination mechanisms to construct ideal SEI layers have become increasingly prevalent in recent years [165–168].

Despite their remarkable efficacy, the practical application of fluorine-containing strategies remains controversial. The introduction of fluorinated components may pose environmental concerns, increase costs, and induce potential side reactions during long-term cycling. These considerations have spurred the exploration of fluorine-free interfacial modulation strategies. Under the background, our team has recently proposed an elastic bridging structural design within fluorine-free polymer electrolytes to regulate the Li^+ coordination environment [169]. Earlier analogous research on fluorine-free GPE conducted by Xu et al. has also demonstrated that rational modulation of the coordination environment can similarly facilitate the formation of a stable SEI layer and suppress dendrite growth without relying on fluorine-containing components [170]. In this system, highly polar cyclic vinyl carbonate serves as the primary coordination site for Li^+ , while the weakly polar cross-linking unit $\text{N,N}'$ -methylenebisacrylamide reduces the electron cloud density of coordinating O atoms through its electron-withdrawing effect. The synergistic interaction between strong and weak coordination promotes the formation of a weakly solvated Li^+ structure, significantly altering the interfacial reaction pathway. Given that the polymer matrix possesses a lower lowest unoccupied molecular orbital (LUMO) level, it undergoes preferential reduction at the lithium metal surface, leading to the formation of an SEI layer predominantly composed of inorganic compounds such as Li_2O and Li_3N . This SEI layer facilitates uniform lithium deposition along the (200) crystallographic plane and effectively suppresses dendrite growth. Owing to the stable SEI layer and the uniform lithium deposition, the assembled full cells maintain 84.7% of their capacity after 800 cycles at a 3C rate.

4.2. Recent development of polymer-based electrolytes focuses on heterogeneous metal cation competitive coordination

In addition to strategies for regulating Li^+ coordination, the coordination effects of numerous transition metal ions have also been extensively utilized to enhance the performance of lithium-based batteries. Selecting different metal cations based on specific research systems and coordination environment requirements represents an effective strategy. Zr^{4+} can form stable coordination bonds with sulfonate groups ($-\text{SO}_3^-$) and ester groups ($-\text{COOR}$), significantly enhancing the mechanical properties of polymer-based electrolytes [171,172]. Similarly, Ni^{2+} can coordinate with imidazole ligands on specific polymer chains. Such coordination interactions form physical crosslinking points, thereby enhancing the elastic modulus of the polymer [173]. However, the formation of these conventional metal complexes may affect the segmental dynamics of the polymer, leading to an increase in the T_g , which is unfavorable for ion migration. In fact, metal-ligand coordination bonds represent a highly unique type of non-covalent interaction with tunable bond energy [174]. By rationally combining metal ions with functional organic ligands, the trade-off between mechanical properties and T_g in metal-containing polymers can be effectively addressed to a certain extent [175]. Zhao et al. designed a structurally novel metal-organic polymer by utilizing molybdenum (Mo) paddlewheel complexes as tetratopic linkers to bridge organic and inorganic moieties at the molecular level [176]. The resulting SPE exhibits exceptional mechanical properties and a low T_g (< 50 °C). Notably, the unsaturated coordination sites of Mo atoms effectively immobilize anions while facilitating Li^+ migration. The polyphenolic compound ellagic acid (EA) exhibits strong chelation with various metal ions through its phenolic hydroxyl groups, enabling the formation of highly ordered and stable metal-organic coordination complexes [177, 178]. Inspired by this, Wu et al. synthesized a polymer nanonetwork

with a highly amorphous structure through the self-assembly of cerium ions and EA, and subsequently incorporated it into the PEO matrix for application in LMB [179]. The strong coordination ability of cerium ions enables it to compete with Li^+ for coordination sites, interacting with the basic O atoms on PEO. This interaction weakens the interaction between PEO and Li^+ , thereby increasing the t_{Li^+} . Furthermore, the assembled symmetric $\text{Li}||\text{Li}$ cell enables a stable cycling at 0.1 mA cm^{-2} for at least 8800 h without short circuit.

Besides the aforementioned heterogeneous metal ions, recent studies have revealed that copper ions can effectively decouple the contradiction between Li^+ transport and the restricted ionic conduction caused by dynamic cross-linking. The coordination environment of copper ions is highly tunable, and its structural flexibility has facilitated the synthesis of diverse mononuclear and polynuclear copper complexes. These properties underscore the exceptional significance of copper ions in coordination chemistry. Typically, Yang et al. introduced Cu^{2+} for coordination with cellulose nanofibrils (CNF), as illustrated in Fig. 10a [180]. This interaction expands the inter-polymer chain spacing into molecular channels, altering the crystalline structure of CNF and thereby accelerating Li^+ transport. Specifically, they also found that Li^+ move along cellulose molecular chains or between cellulose molecular chains, while the main chain of cellulose moves very little, indicating that the jumping of Li^+ is decoupled from the movement of polymer chains. Inspired by this, Wang and Wei et al. introduced Cu^{2+} to promote Li^+ dissociation by immobilizing anions and leveraged the strong coordination between Cu^{2+} and O to weaken the Li-O interaction, thereby accelerating Li^+ transport (Fig. 10b,c) [181,182]. In addition, Hu et al. also introduced copper ions as catalytic centers into the gel polymer framework, where they coordinated with carboxyl groups to be immobilized throughout the gel matrix, thereby accelerating cation deposition and migration [183]. Similar work includes the copper maleate hydrate SPE synthesized by Zhan et al. [184] This electrolyte features highly ordered one-dimensional channels interconnected by $\text{Cu}^{2+}/\text{Cu}^+$ nodes and maleate ligands (as shown in Fig. 10d). These channels enable rapid Li^+ transport through a combination of ion-hopping and coupled dissociation-association mechanisms, demonstrating an exceptional ionic conductivity (1.17×10^{-4} S cm^{-1}), a high t_{Li^+} (0.77), and a wide EW of 4.7 V.

4.3. Recent development of polymer-based electrolytes focuses on organic cation co-coordination

Organic cation co-coordination refers to a strategy that optimizes Li^+ transport kinetics and interfacial stability by introducing various organic cations (e.g., quaternary ammonium salts, imidazolium-based cations, and pyrrolidinium-based cations) to modulate the solvation structure of Li^+ and its interface behavior within polymer-based electrolytes. The coordination ability of these organic cations is primarily determined by their molecular topological structures [185,186]. Quaternary ammonium salts, such as tetraethylammonium, exhibit a tetrahedral geometry with uniformly distributed charges and significant steric hindrance. These cations preferentially coordinate with anions through electrostatic interactions, thereby weakening the Li^+ -anion interactions and enhancing the t_{Li^+} [187,188]. Imidazolium-based cations, such as 1-ethyl-3-methylimidazolium, feature a planar conjugated structure with charges concentrated on the nitrogen atoms of the imidazole ring. These cations exhibit both π - π stacking interactions and hydrogen bonding capabilities, enabling simultaneous coordination with anions and solvent molecules [85,189].

In fact, the application of organic cation coordination strategies has primarily been confined to ionic liquid-based electrolytes [190–194]. Yu et al. selected different IL to modulate the solvation environment of Li^+ [195]. The key of their approach lies in the varying interaction strengths between different organic cations and solvent molecules as well as anions (Fig. 11a). But in the field of polymer-based electrolytes, relevant strategies have rarely been reported. Recently, Our team has previously

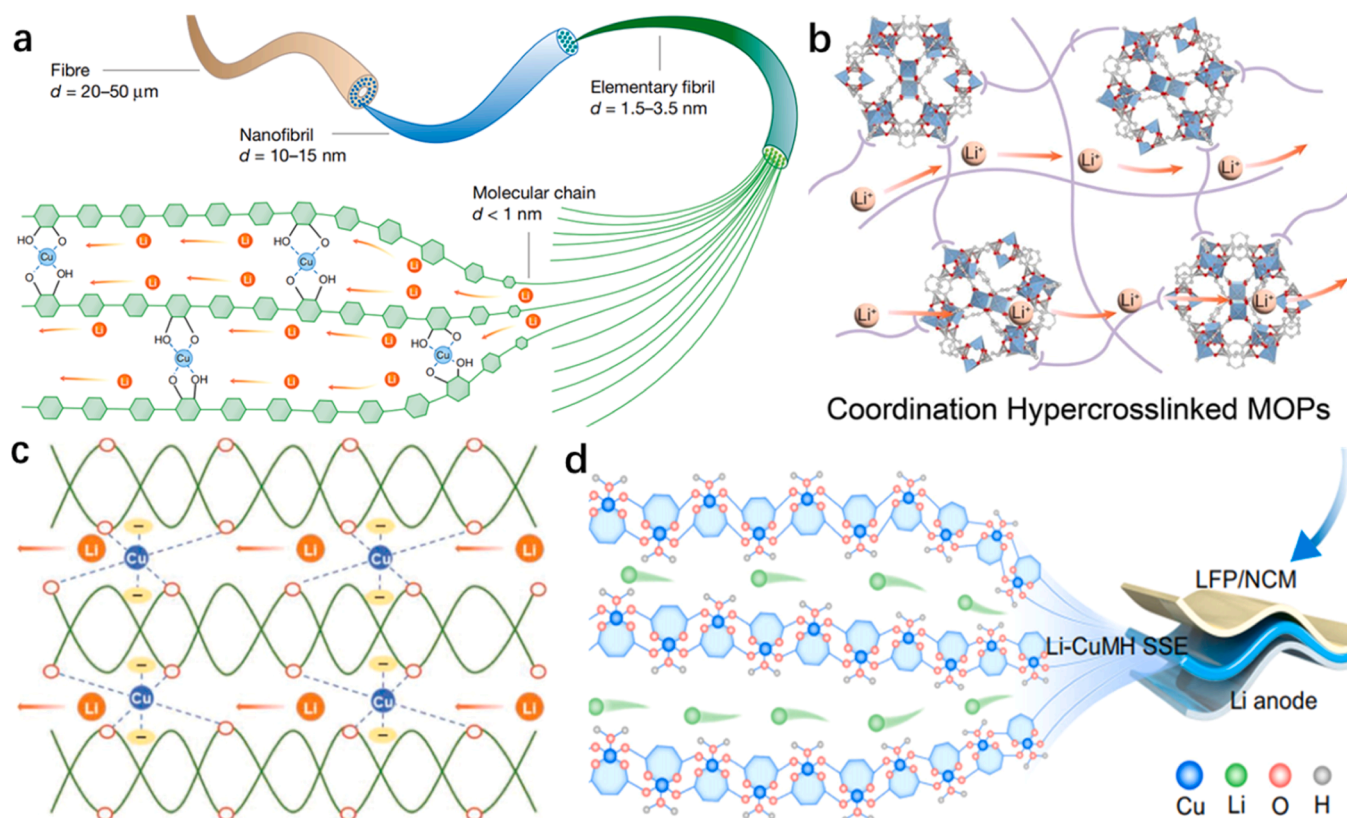


Fig. 10. a) Coordination between Cu^{2+} and CNF broadens the Li^+ transport channels. Reproduced with permission [180]. Copyright 2021, Springer Nature. b, c) Cu^{2+} coordination immobilizes anions and accelerates Li^+ transport. Reproduced with permission [181,182]. Copyright 2024 and 2023, respectively, Wiley-VCH. d) Coordination leads to the formation of highly ordered channels. Reproduced with permission [184]. Copyright 2024, Springer Nature.

proposed an organic cation co-ordination strategy [134]. As illustrated in Fig. 11b, the introduction of IL promotes the dissociation of lithium salt. Meanwhile, the N-butyl-N-methylpyrrolidinium (Pyr^+_{14}) compete with Li^+ for coordination with polar groups on the polymer chains, occupying polymer coordination sites and compelling Li^+ to bind with more TFSI $^-$, thereby forming an anion-rich solvation structure. Additionally, the coordination of Pyr^+_{14} with $\text{C}=\text{O}$ groups and fluorinated functionalities in the polymer chains expands the interchain spacing, providing pathways for high-speed Li^+ transport. A similar competitive coordination strategy was also adopted by Lee's team, albeit with different coordination targets [196]. As illustrated in Fig. 11c, their proposed weakly coordinating cationic polymer electrolyte regulates the Li^+ coordination environment through two mechanisms: First, the imidazolium-based cationic polymer matrix competes with SN for Li^+ coordination, weakening the Li^+ -SN interaction and promoting Li^+ decoordination. Second, at the electrode-electrolyte interface, anion repulsion effects during charging induce a unique Li^+ coordination structure, further reducing the Li^+ coordination energy. This dual-regulation mechanism enables solid-state LMB to achieve an impressive room-temperature ionic conductivity of $1.46 \times 10^{-4} \text{ S cm}^{-1}$ and a t_{Li^+} of 0.88.

As previously mentioned, IL can serve as plasticizers and modulate the coordination environment. Zhou et al. introduced imidazolium IL end groups bearing a fluorinated alkyl chain into a GPE [197]. The imidazolium cations can anchor TFSI $^-$ onto the polymer backbone through electrostatic interactions. Meanwhile, the synergistic effect with fluorine atoms reduces the coordination strength between Li^+ and the O atoms in the polymer chains, facilitating easier migration of Li^+ . Accordingly, it realized a high Li^+ conductivity ($9.16 \times 10^{-3} \text{ S cm}^{-1}$) and t_{Li^+} of 0.69. Similarly, Dong et al. copolymerized poly-tetramethylene ether glycol (PTMEG) and vinyl imidazolium IL to form crosslinked ionic copolymer solid electrolytes [198]. The repeating units of the

PTMEG segments contain more carbon atoms than those in PEO, resulting in a looser Li coordination structure (Fig. 11d). Meanwhile, the imidazolium cations act as fixed Lewis acids, attracting TFSI $^-$ and promoting the dissociation of lithium salt, thereby further enhancing the effective migration fraction of Li^+ . As a result, The t_{Li^+} increased from 0.36 to 0.47 upon the addition of IL, while the EW expanded from 4.7 V to 5.1 V.

4.4. Recent development of polymer-based electrolytes focuses on harnessing anion coordination

The preceding discussion has highlighted the pivotal role of cationic coordination in the ion transport mechanisms of polymer-based electrolytes. In fact, the behavior and interactions of anions are equally critical. Understanding the mechanistic role of "anion coordination" and its judicious application can further guide the construction of high-performance polymer-based electrolytes. Obviously, substantial differences exist between anions and transition metals. The term of anion coordination is rarely invoked. —anions, like transition metals, exhibit "secondary valence states" (where electrons flow from electron-rich anions [coordination centers] to hydrogen bond donors [ligands]). Anions not only demonstrate variable coordination numbers (i.e., the number of hydrogen bonds formed between anions and acceptors) but also adhere to specific coordination geometries. Actually, anions can also exhibit "secondary valence states" similar to transition metals, where electrons flow from electron-rich anions (coordination centers) to hydrogen bond donors (ligands). Anions not only demonstrate different CN (i.e., the quantity of hydrogen bonds formed between anions and acceptors), but also adhere to specific coordination geometries [199, 200]. In polymer-based electrolytes, anion coordination typically refers to the interactions between anions and Li^+ , polymer chains, or other additives. Unlike Li^+ , which often coordinate directly with polymer

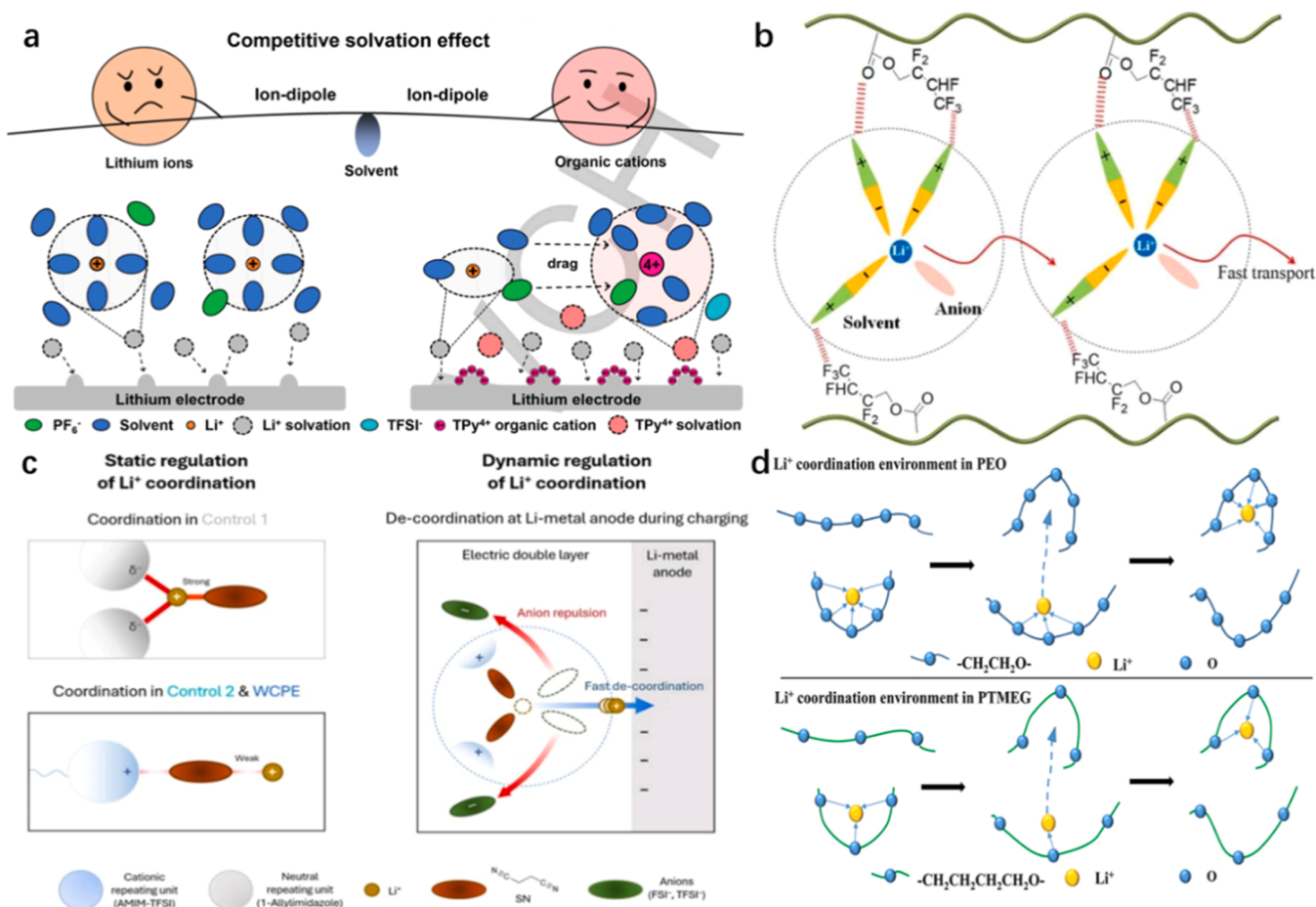


Fig. 11. a) Scheme of organic cations regulated Li solvation. Reproduced with permission [195]. Copyright 2025, Wiley-VCH. b) Solvation structure and interaction model in PE. Reproduced with permission [134]. Copyright 2024, Wiley-VCH. c) Two regulations of Li^+ coordination. Reproduced with permission [196]. Copyright 2025, Wiley-VCH. d) Schematic illustration of the loose coordination structure of PTMEG compared to PEO. Reproduced with permission [198]. Copyright 2021, Elsevier.

chains (e.g., the EO units in PEO), anions in many systems exhibit limited direct coordination with polymers, resulting in their relatively high mobility. For instance, in PEO-based electrolytes, Li^+ are encased within the helical structure of PEO chains, while anions generally remain in the outer regions, maintaining a relatively free state. This free mobility leads to a low t_{Li^+} , indicating that the majority of the current is carried by anions rather than Li^+ . Such behavior of anions can induce concentration polarization and lithium dendrite growth, thereby compromising battery safety and cycle life.

As discussed in the previous section regarding the advantages of IL in polymer-based electrolyte applications, past studies have explored the addition of TFSI-based IL as plasticizers to PEO-based electrolytes to prepare ternary SPE [201,202]. TFSI⁻ is a commonly employed weakly coordinating anion that enhances ionic conductivity due to its low lattice energy and high degree of dissociation. While the overall conductivity improves, this enhancement primarily stems from the plasticizing effect that increases the mobility of PEO chain segments. Given the weak interaction between TFSI⁻ and Li^+ , the predominant transport mode of Li^+ remains along the PEO chains [38]. It does not address the "free behavior" of anions. To overcome the limitations of Li^+ transport mechanisms in conventional ternary SPE, researchers have recently shifted their focus to the design and regulation of anions in IL, aiming to achieve fundamental optimization of Li^+ migration. Trifluoromethanesulfonyl-N-cyanoamide (TFSAM) is an asymmetric anion that integrates the strong electron-withdrawing group ($-\text{SO}_2\text{CF}_3$) from TFSI⁻ and a more polar and coordinatively capable $-\text{CN}$ group. This structural combination enables Li^+ to form the monodentate

coordination with the $-\text{CN}$ group, even at low Li^+ concentrations [203, 204]. The team of Elie Paillard selected TFSAM-based IL to fabricate ternary SPE and investigated the "anion-assisted" transport mechanism [205]. Through MD simulations and RS, they demonstrated that TFSAM, with its strong coordinative ability, competes with PEO for Li^+ coordination via the $-\text{CN}$ group. This competition enables some Li^+ to break free from the "constraints" of the EO units linkages and "hitch a ride on the TFSAM anion express" (Fig. 12a). This fundamentally breaks through the limitations of Li^+ transport modes in conventional PEO-based electrolytes, significantly accelerating Li^+ transport (increases t_{Li^+} by a factor 6 and the Li^+ conductivity by 2–3). Meanwhile, this discovery also broadens the scope of anion selection: contrary to the traditional view that weakly coordinating anions are the optimal choice for polymer-based electrolytes, many strongly coordinating anions, previously dismissed due to insufficient dissociation, actually exhibit significant potential.

4.4.1. Regulation and guidance of anions

In polymer-based electrolytes, anions serve as indispensable charge carriers, and their physicochemical properties exert a profound influence on the electrolyte's microstructure, macroscopic performance, as well as the characteristics of electrode-electrolyte interphases/interfaces [209]. Anions play a complex yet pivotal role in polymer-based electrolytes, with both positive and negative impacts. Certain anions, such as FSI⁻, TFSI⁻, and BF₄⁻, facilitate the formation of more stable and lower-resistance SEI layers. Additionally, employing anions with higher oxidative and chemical stability, such as TFSI⁻ compared to PF₆⁻, can

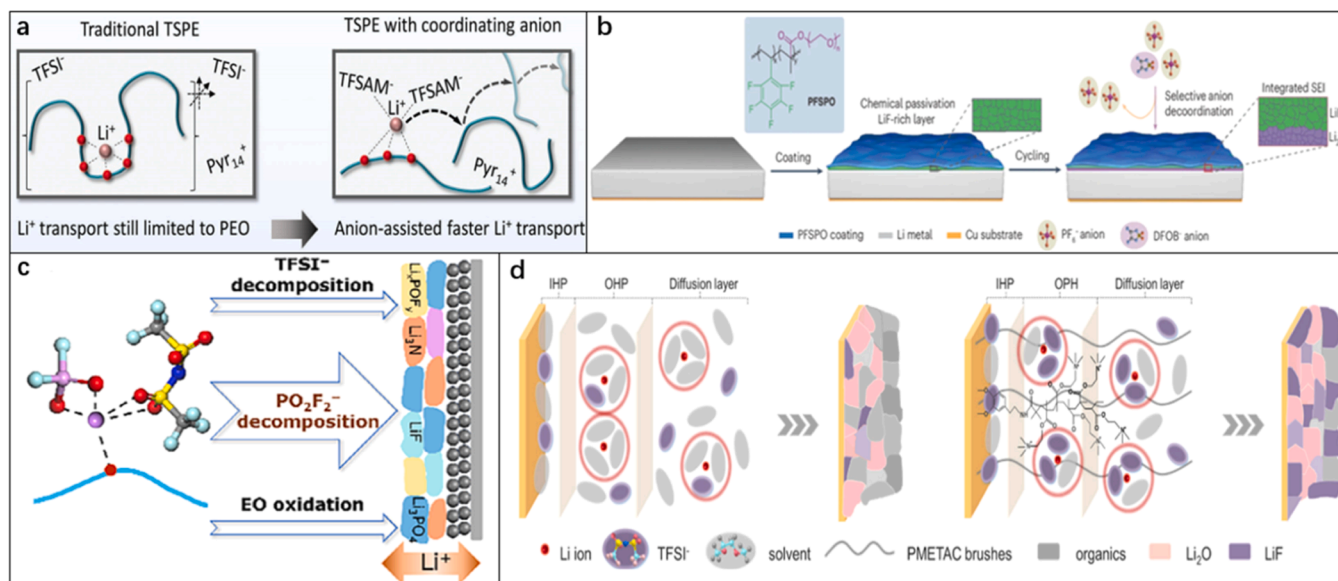


Fig. 12. a) The coordination between Li⁺ and TFSAM anions alters the ion transport mechanism in SPE. Reproduced with permission [205]. Copyright 2022, Wiley-VCH. b) Schematic illustrations of the progressive dual-passivation coating strategy to form an integrated SEI for stabilizing Li-metal anode. Reproduced with permission [206]. Copyright 2025, Springer Nature. c) Schematic of anion decomposition at the LiCoO₂/SEI interface after cycling. Reproduced with permission [207]. Copyright 2025, Wiley-VCH. d) Polymer brushes regulate the anions. Reproduced with permission [208]. Copyright 2024, Royal Society of Chemistry.

broaden the EW of the electrolyte, enabling compatibility with high-voltage cathode materials. As a commonly used lithium salt in commercial electrolytes, LiPF₆ exhibits excellent low-temperature conductivity and SEI film-forming capabilities, along with good solubility in most solvents. However, PF₆⁻ is prone to hydrolysis in the presence of trace amounts of water, generating hydrofluoric acid (HF), which leads to corrosion of the cathode active materials and aluminum current collectors [210]. To suppress corrosion issues while fully leveraging the advantages of LiPF₆, Li et al. synthesized a copolymer containing EO units, namely poly(pentafluorostyrene)-co-(poly(ethylene glycol) methyl ether methacrylate) (PFSPPO) [206]. In a dual-salt electrolyte comprising LiPF₆ and lithium bis(oxalato)borate (LiDFOB), the EO units preferentially coordinate with Li⁺ through strong interactions, weakening the interaction between PF₆⁻ and Li⁺ while minimally affecting DFOB⁻. As shown in Fig. 12b, this selective coordination causes PF₆⁻ to dissociate from the Li⁺ solvation sheath and be excluded from the electrode/electrolyte interface, whereas DFOB⁻ becomes enriched at the interface and preferentially decomposes to form an inner SEI layer dominated by Li₂O (exhibiting high ionic conductivity and mechanical stability). Simultaneously, the pentafluorophenyl groups from PFSPPO spontaneously react with lithium metal to generate an outer SEI layer dominated by LiF (chemically inert and effective at blocking side reactions). As a result, this coordination strategy remarkably enhances the stability of Li metal anodes, enabling double-layer Li||NMC811 pouch cells to maintain 80% capacity after 611 cycles under a low electrolyte/capacity (E/C) ratio of 2.0 g Ah⁻¹. Removing LiPF₆ and using LiDFOB alone would drastically increase costs while reducing ionic conductivity. This selective anion decoordination strategy enables the construction of a robust integrated SEI structure at significantly lower costs, offering an advanced approach: proactively and selectively harnessing the advantages of anions rather than passively accepting their drawbacks. Wang et al. also focused on the regulation of dual-salt anions, selecting LiDFOB and lithium tetrafluoroborate (LiBF₄) for their study [211]. Kong et al. proposed that introducing an anion with stronger Li⁺ coordination capability than TFSI⁻ would weaken the positive charge on Li⁺, thereby dampening its interaction with polymer chains and facilitating Li⁺ migration (Fig. 12c) [207].

In the field of CPE, the multiple coordination interactions between Li⁺, various anions, and polymer chain segments lead to ambiguous ion

conduction pathways. Moreover, when solvents were introduced, the motion of ionic clusters (composed of Li⁺, anions, and solvent molecules) involves multiple components, making it difficult to determine which component predominantly governs ionic conduction and interfacial reactions. To address this issue, Fan et al. designed a thin-film polymer/Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂(LLZTO) CPE [212]. By introducing triethylene glycol dimethyl ether (TGDE) and LiDFOB, specific ionic clusters were formed. Through the regulation of the coordination interaction between DFOB⁻ anions and TGDE, the primary carrier within the ionic clusters was clearly identified, eliminating the complexity associated with ionic cluster dynamics. This facilitated uniform Li⁺ deposition and the formation of a stable SEI, achieving stable cycling of symmetric Li||Li cell at 0.2 mA cm⁻² for over 2000 h. Meanwhile, the coordination between DFOB⁻ anions and TGDE significantly "constrained" the strong interactions between Li⁺ and anions, leading to the explicit "confined ionic transport channels." Obviously, employing specific strategies to regulate and guide anion behavior is an effective approach for optimizing ionic transport. Li et al. also ingeniously employed polymer brushes to achieve precise regulation of anions [208]. The core idea lies in the positively charged quaternary ammonium groups on the polymer brushes, which can attract anions through electrostatic interactions, leading to anion enrichment at the nanoscale interface. Meanwhile, the steric hindrance effect of the polymer brushes isolates solvents from the first inner solvation shell of Li⁺. As illustrated in Fig. 12d, under the synergistic regulation of these two mechanisms, the nanoscale interfacial solvation structure is optimized and reconstructed, promoting more anions to participate in the solvation coordination of Li⁺. The unique interfacial regulation mechanism facilitates the formation of a stable, inorganic-rich SEI on the electrode surface.

4.4.2. Fixation of anions for decoupled ion transport

In addition to regulating anion solvation behavior and interfacial distribution, directly fixing anions onto the polymer backbone has emerged as a particularly effective strategy for fundamentally reconstructing ion transport pathways. In most conventional polymer-based electrolytes, ion transport remains fundamentally governed by the coupled ion transport mechanism. The migration process of Li⁺ does not occur independently; rather, it is interrelated with or constrained by the movements of other ions, polymer chain segments, and solvation

structure rearrangements [213]. This coupling relationship fundamentally restricts the enhancement of t_{Li^+} , particularly under low-temperature or high-rate conditions. Consequently, decoupled ion transport systems have emerged as a critical research focus in the development of advanced polymer-based electrolytes.

From the perspective of coordination chemistry, the essence of decoupled ion transport lies in mitigating the kinetic dependence of Li^+ migration on long-range polymer chain segmental rearrangements. This objective can be achieved through two primary strategies: constructing fixed coordination sites to facilitate directional Li^+ hopping, and introducing dynamically reconfigurable weak coordination environments to continuously reduce migration energy barriers [214,215]. The coordination strategies introduced previously, such as competitive cation coordination and weak solvation design, can be regarded as effective approaches to achieving decoupled ion transport. In addition, anion immobilization can reconstruct the local coordination environment of Li^+ by introducing and stabilizing negatively charged sites within the polymer matrix. Consequently, Li^+ is enabled to continuously hop between adjacent coordination centers without relying on large-scale segmental relaxation of the polymer chains. This renders single-ion conductive polymer electrolytes (SICPE) a representative system for decoupled ion transport, which has garnered increasing attention in recent years [216–219].

Ding et al. conducted a detailed comparison between SICPE and traditional dual-ion conducting polymer electrolyte [220]. The free anions in dual-ion conducting polymer electrolyte lead to severe concentration polarization, readily inducing the formation of lithium dendrites under high current conditions. In contrast, the SICPE achieves the fixation of anions by covalently bonding anions to the polymer backbone, resulting in a higher t_{Li^+} of 0.75 and favorable electrochemical stability. More significantly, the immobilized anionic groups function as

well-ordered hopping sites for Li^+ , facilitating its transport via exchange between adjacent coordination sites. By covalently anchoring these anionic groups onto the polymer backbone, the migration of anions can be effectively suppressed, thereby mitigating concentration polarization and enhancing the t_{Li^+} . However, in traditional SICPE, the common anions (e.g., $-\text{COO}^-$ or $-\text{SO}_2\text{N}^-\text{SO}_2^-$) possess concentrated negative charges, which form strong electrostatic interactions with Li^+ . This results in low ionic conductivity, which is detrimental to the cycling stability of the battery [221]. Obviously, it does not align with our expectations for highly efficient decoupled ion transport. Therefore, recent research efforts have shifted from merely immobilizing anions to precisely engineering the local coordination environment surrounding anchored anionic sites [222]. Xu et al. further designed a covalent organic framework (COF) modified SICPE, establishing a decoupled ion transport network [223]. As shown in Fig. 13a, with anions immobilized, the electron-withdrawing cyano groups on the COF significantly reduce the dissociation energy barrier of lithium salts through ion-dipole interactions, thereby releasing Li^+ from anionic constraints. The free Li^+ rapidly migrate along the synergistic ion transport pathways between the COF and the SICPE. This approach ultimately achieves markedly enhanced ionic conductivity ($9.2 \times 10^{-4} \text{ S cm}^{-1}$) and an exceptionally high t_{Li^+} (0.94).

4.4.3. Fixation of anions by zwitterionic

Unlike SICPE, which suffer from the difficulty in cation decoupling caused by the strong influence of anions with high negative charge density, zwitterions with both cations and anions coexisting in a single molecule, have attracted widespread attention [224]. The strong coupling between the positive and negative charges on the backbone of zwitterionic polymers leads to the formation of stable "ion pairs". Moreover, due to the strong electrostatic interactions between

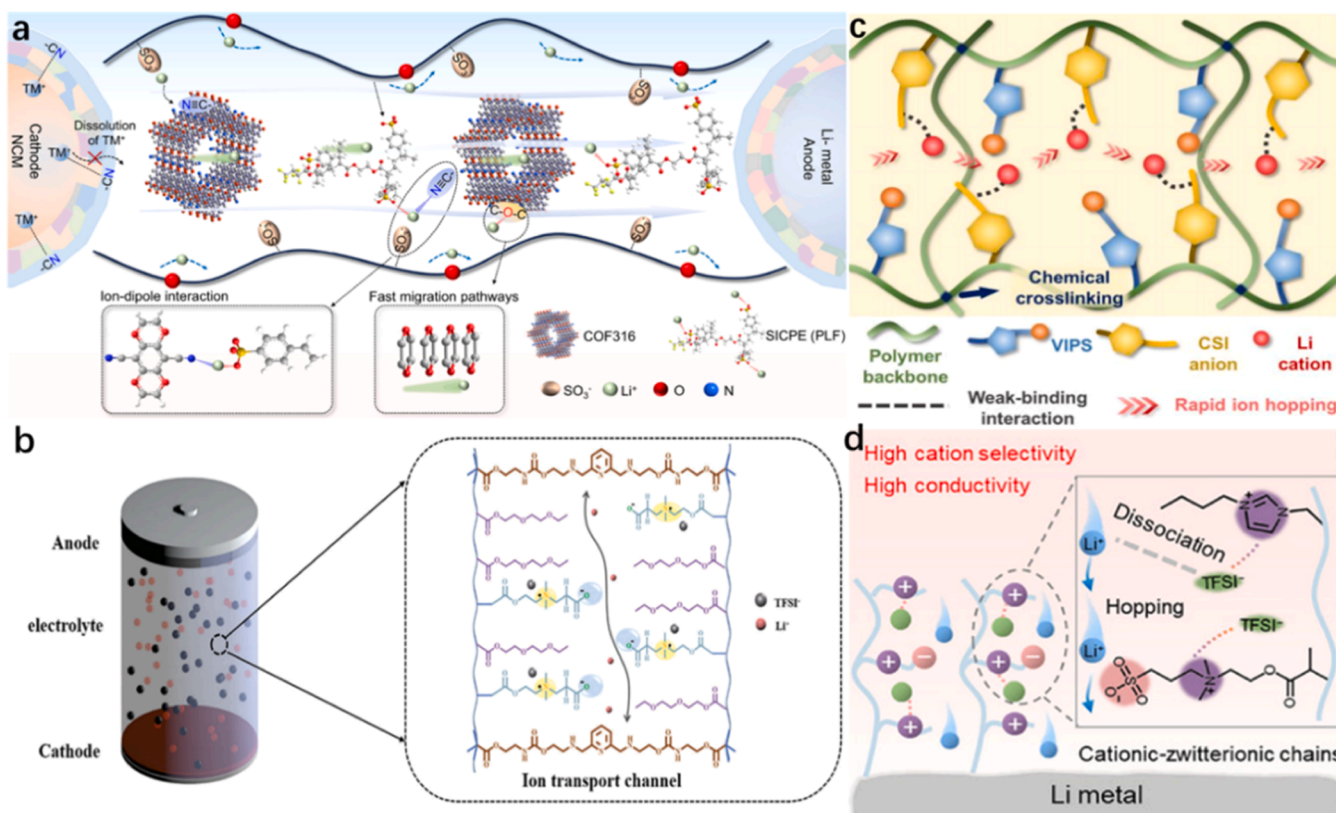


Fig. 13. a) Regulation mechanisms of COF on the decoupled ion transport of SICPEs. Reproduced with permission [223]. Copyright 2025, American Chemistry Society. b) Schematic structure of ZPE with fishing-net-like structure and possible transport mechanism of Li^+ in the interior. Reproduced with permission [225]. Copyright 2023, Wiley-VCH. c) Weak-binding interaction and rapid Li^+ hopping through ion channel formed. Reproduced with permission [226]. Copyright 2025, Wiley-VCH. d) Schematic of anion immobilization by cationic-zwitterionic polymer chains. Reproduced with permission [227]. Copyright 2025, Wiley-VCH.

zwitterionic groups and anions, the movement of anions is significantly restricted. Their team once designed a zwitterionic polymer electrolyte (ZPE) to regulate the transmission of ions [225]. As shown in Fig. 13b, the zwitterionic groups of CBMA can form high molecular dipole moments. These high dipole moments can enhance the dielectric properties of the electrolyte and reduce the coordination strength between Li^+ and anions, thereby accelerating the dissociation of lithium salt. Additionally, due to electrostatic effects, the movement of anions is immobilized by the zwitterionic groups, making Li^+ the primary charge carrier.

While scientists were still engaged in comparing the merits and drawbacks of SICPE and ZPE, Yun's team ingeniously integrated a weak-binding monomer (LiCSI) and a high-dipole zwitterionic monomer (VIPS) into a single system [226]. As illustrated in Fig. 13c, the LiCSI contains -CN and aromatic rings that delocalize electron density, dispersing the negative charge around Li^+ and reducing the Li^+ binding energy. VIPS covalently anchor the anions to the polymer backbone, also making Li^+ become the primary mobile charge carrier. This configuration minimizes anion accumulation at the electrode/electrolyte interface and lowers concentration polarization. A relatively detailed review of this part of the work already exists, so it will not be elaborated on further here. Employing a similar principle, Xiao et al. opted to in-situ polymerize an ionic liquid with a zwitterionic monomer, yielding a Cationic-ZPE [227]. As depicted in Fig. 13d, the $-\text{SO}_3^-$ groups preferentially coordinate with Li^+ , facilitating the dissociation of lithium salts. Under the synergistic effect of zwitterions and cations from the IL, the objective of immobilizing anions was further achieved. This approach maintained a t_{Li^+} of 0.72 while attaining a room-temperature ionic conductivity of $1.6 \times 10^{-3} \text{ S cm}^{-1}$.

5. Extended applications of coordination chemistry

5.1. Emerging coordination methods

Besides the conventional coordination routes described above, several non-traditional strategies also deserve attention, which open the new directions for polymer-based electrolyte design.

5.1.1. Solvation clusters and their coordinated migration

PVDF is a widely used polymer matrix, and previous studies have demonstrated that residual solvents are inevitably present in PVDF-based polymer electrolytes [228]. Taking N,N-dimethylformamide (DMF) as an example, due to the strong interaction between Li^+ and DMF, conventional desolvation methods (e.g., heating) cannot completely remove residual DMF. Interestingly, solvent retention is not necessarily detrimental—DMF promotes lithium salt dissociation and plays a crucial role in ionic conduction. MD simulations reveal that, on average, each Li^+ coordinates with three anions and one DMF solvent molecule to form solvation clusters [228]. These clusters act as the primary charge carriers, differing from the conventional mechanisms in SPE or GPE, where Li^+ typically migrates via chain hopping or along polymer segments. Zhang et al. further validated this observation and improved the solvent system to optimize performance [229]. To address the irreversible side reactions between DMF and lithium metal, 2,2,2-trifluoro-N,N-dimethylacetamide (FDMA) was employed as an alternative solvent, together with poly(vinylidene fluoride-hexafluoropropylene) (PVHF) as the polymer matrix. The strong electron-withdrawing $-\text{CF}_3$ group in FDMA lowers its LUMO energy level, enhancing its reduction stability. Even minor reduction on the Li surface forms a beneficial LiF -rich SEI layer. The stable SEI layer enables the $\text{Li}||\text{LFP}$ cell retaining 80.3% of its initial capacity even after 2500 cycles at 1 C. Li^+ forms solvation clusters denoted as Li-FDMA-3TFSI^- , within which molecular dynamics simulations reveal weak coordination between Li^+ and the O atoms of TFSI^- , rather than with F atoms in PVHF. This distinctive coordination enables Li^+ to migrate rapidly along the polymer chains as part of the solvation cluster, resembling a rolling sphere (Fig. 13a).

5.1.2. High-entropy coordination for faster transport

The enhancement of thermal stability, mechanical robustness, and ionic conductivity of polymer-based electrolytes remains a critical focus for researchers. In recent years, the high-entropy polymer electrolytes design strategy has garnered significant attention [230,231]. Ye et al. employed polyethyleneimine (PEI), rich in $-\text{NH}_2$ groups, as a ligand and covalently anchored PVHF onto PEI backbones through a click-like reaction, yielding a highly disordered high-entropy SPE architecture [232]. As illustrated in Fig. 14b, the disordered structure creates abundant Li^+ transport pathways, overcoming limitations inherent to conventional copolymerization/crosslinking strategies. As previously noted, the coordination environment exerts a critical influence on Li^+ transport behavior. Extending beyond high-entropy polymer chains, Yang et al. focused on enhancing the coordination entropy of Li^+ by introducing four types of lithium salt to fabricate a high-coordination-entropy SPE, thereby increasing the diversity or disorder of the coordination environment surrounding Li^+ [233]. Compared to the control single-salt SPE, the incorporation of different anions significantly weakened the interaction between Li^+ and the polymer chains, as illustrated in Fig. 14c. The high-coordination-entropy SPE not only exhibited the highest ionic conductivity and t_{Li^+} but also demonstrated the highest exchange current density, indicating the fastest Li^+ transport kinetics. Wang et al. further introduced the thermodynamic parameter enthalpy to represent the strength of coordination interactions [234]. Their validation confirmed that a low-enthalpy and high-entropy configuration represents the optimal model for Li^+ coordination with polymer chains (mobile cations), whereas a high-enthalpy and low-entropy configuration is optimal for anion coordination (fix anions). This work essentially aligns with the design strategy of high-entropy polymers electrolytes.

5.1.3. Artificial intelligence

With the advancement of artificial intelligence (AI), its applicability has progressively extended across diverse research domains [235,236]. For the rapidly evolving field of secondary solid-state batteries, AI-driven methodologies have emerged as transformative tools. Historically, materials exploration relied on exhaustive trial-and-error combinations—a resource-intensive process. Machine learning (ML) and neural network algorithms, serving as foundational branches of AI, can significantly accelerate the discovery of advanced solid-state battery materials [237,238]. Lao et al. designed a Hofmann complex featuring two-dimensional Li^+ conduction channels [239]. In this system, DMF molecules on the Hofmann coordination framework act as ligands, interacting with tunable metal sites within the complex to modulate the Li^+ coordination environment. As illustrated in Fig. 15a, by using unsupervised learning and Climbing Image-Nudged Elastic Band (CI-NEB) simulations to optimize metal sites, a suitable weak-coordination environment was identified, significantly reducing experimental workload. Specifically, the advantage of unsupervised learning lies in its ability to autonomously classify input data without manual labeling, thereby uncovering implicit correlations between "weak-coordination" or "strong-coordination" configurations and ionic migration barriers. This approach provides an efficient strategy for designing advanced polymer-based electrolytes [240].

Additionally, supervised learning represents another widely utilized tool in ML [241]. Acting as an experienced "research assistant", it analyzes known "training datasets" (e.g., compositional, structural, and performance data of existing polymer-based electrolytes) to learn and predict potential outcomes of ionic coordination behaviors in novel electrolyte formulations. This capability significantly accelerates and optimizes the design of polymer-based electrolytes, particularly in understanding and regulating ionic coordination mechanisms. It is well recognized that the redox potential serves as a crucial indicator for evaluating the stability of electrolytes. However, current methods face challenges in efficiently and accurately predicting the potential variations of Li^+ under different coordination environments [242,243]. Yang

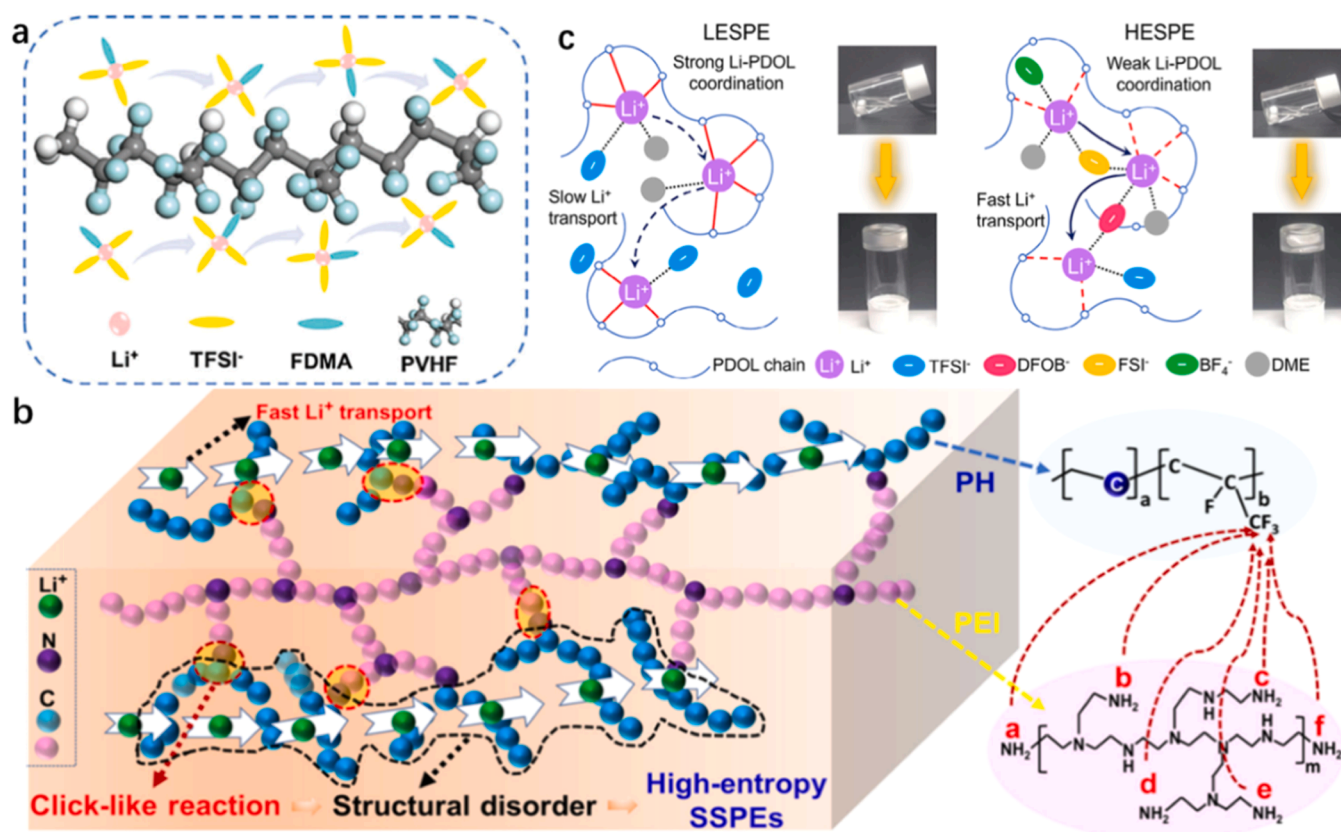


Fig. 14. a) Rational utilization of residual solvent coordination to promote Li^+ transport. Reproduced with permission [229]. Copyright 2024, Wiley-VCH. b, c) High-entropy coordination design strategy. Reproduced with permission [232,233]. Copyright 2024 and 2025, American Chemistry Society and Wiley-VCH, respectively.

et al. employed a supervised learning algorithm to construct a database comprising 140 electrolyte molecules, aiming to predict the lithium-coordinated redox properties (Fig. 15b) [244]. The research findings reveal that the coordination of Li^+ leads to an average increase of 0.60 V in the oxidative potential and an average increase of 0.71 V in the reduction potential. Moreover, this study clarifies the governing patterns, where electronic features predominantly influence the oxidative process, while structural features predominantly influence the reduction process. Gao et al. combined an optimized ML predictive model with DFT calculations to predict the donor numbers of various polymer monomers (Fig. 15c) [245]. Subsequently, they systematically analyzed the coordination capacity between polymers and Li^+ , enabling the efficient design of high-performance polymer-based electrolytes. These studies above demonstrate the advantages brought by the rational utilization of AI in the design and application of coordination mechanisms. Looking forward, as computational power escalates, algorithms continue evolving, and material databases grow increasingly comprehensive, AI is poised to drive transformative progress in the development of solid-state rechargeable batteries.

5.2. Beyond Li^+ coordination

Beyond lithium-ion batteries, the polymer-based electrolyte has also been extensively applied to other rechargeable battery systems—such as sodium and zinc batteries—which are characterized by resource abundance, low cost, inherent safety, and high theoretical capacity [246, 247]. This broad applicability stems from the ability of polymer-based electrolytes to suppress dendrite growth, stabilize electrode/electrolyte interfaces, and mitigate side reactions. This is critically dependent on the regulation of complex coordination interactions

among the various components of the polymer-based electrolyte. Although the core of this review focuses on lithium-based battery, the fundamental principles of coordination chemistry are of universal applicability. It is thus necessary to further briefly explore the applications of coordination chemistry in other emerging battery systems. There are two main purposes for doing so. Firstly, by investigating the coordination behaviors of ions with different sizes and charges (e.g., Na^+ and Zn^{2+}), we can test and expand the universality of the design principles summarized from lithium-based battery studies. Secondly, the unique challenges faced by these non-lithium systems and the corresponding countermeasures can offer new inspiration and ideas for the design of polymer-based electrolytes for lithium-based battery, enabling cross-disciplinary references. Therefore, discussions on these systems contribute to the construction of a more comprehensive and integrated framework for the coordination chemistry of polymer-based electrolytes.

5.2.1. Coordination chemistry of polymer-based electrolytes in sodium batteries

Sodium and lithium both belong to the alkali metal group and exhibit similar physicochemical properties. In sodium battery systems, similar coordination strategies have also begun to attract people's attention. However, sodium ions (Na^+) possess a larger ionic radius (i.e., 1.02 Å and 0.76 Å for Na^+ and Li^+ , respectively) and weaker Lewis acidity compared to Li^+ . On one hand, this results in typically higher migration energy barriers for Na^+ within crystal lattices. On the other hand, it leads to a looser solvation sheath structure for Na^+ , with weaker binding ability toward anions [248]. For the reasons mentioned above, polymer-based electrolytes in sodium battery systems usually combine polymers with organic solvents or plasticizers. For example, SN is a

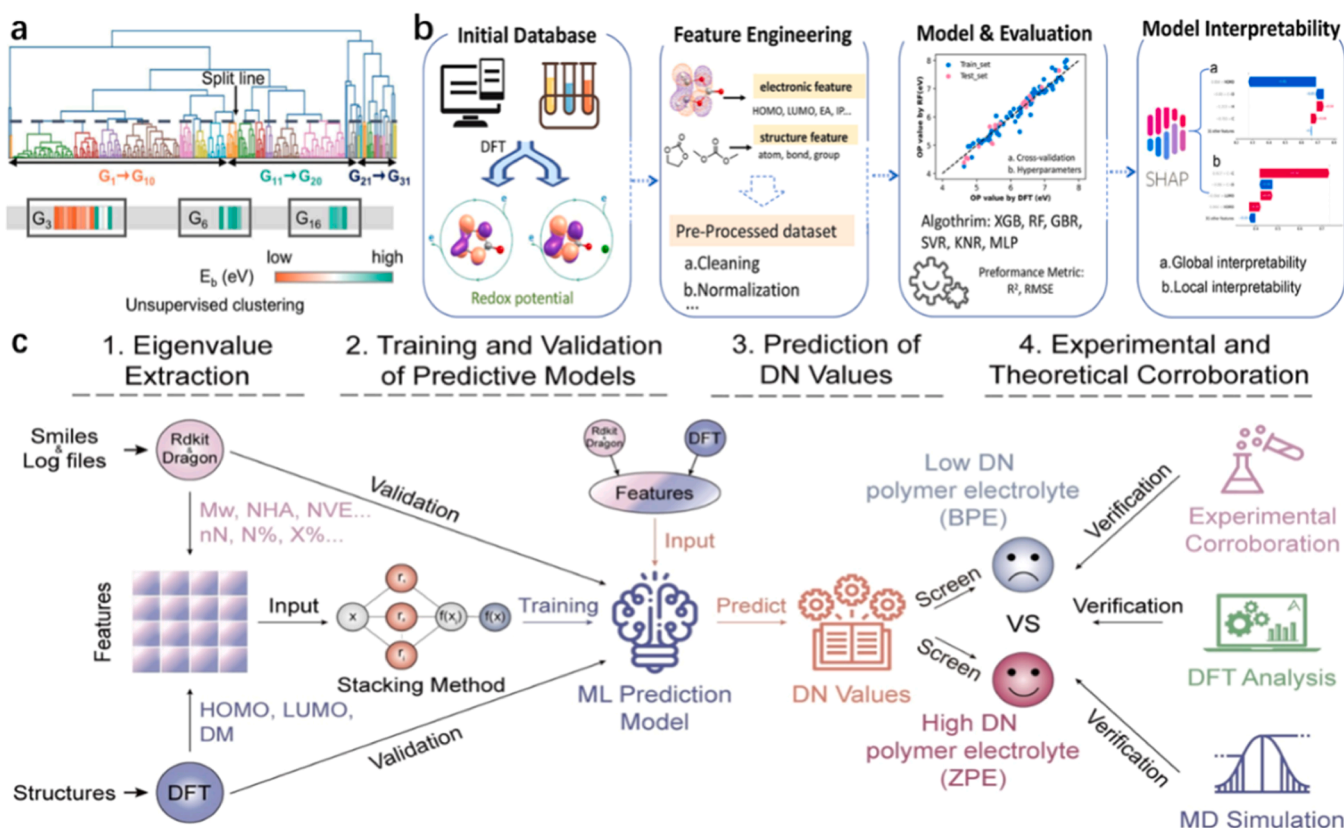


Fig. 15. a) Dendrogram of unsupervised learning algorithm where all Hofmann complexes are divided into 31 groups. Reproduced with permission [239]. Copyright 2025, Springer Nature. b) Workflow of ML for the redox potential prediction. Reproduced with permission [244]. Copyright 2025, Elsevier. c) The design of advanced SPE by ML. Reproduced with permission [245]. Copyright 2025, Wiley-VCH.

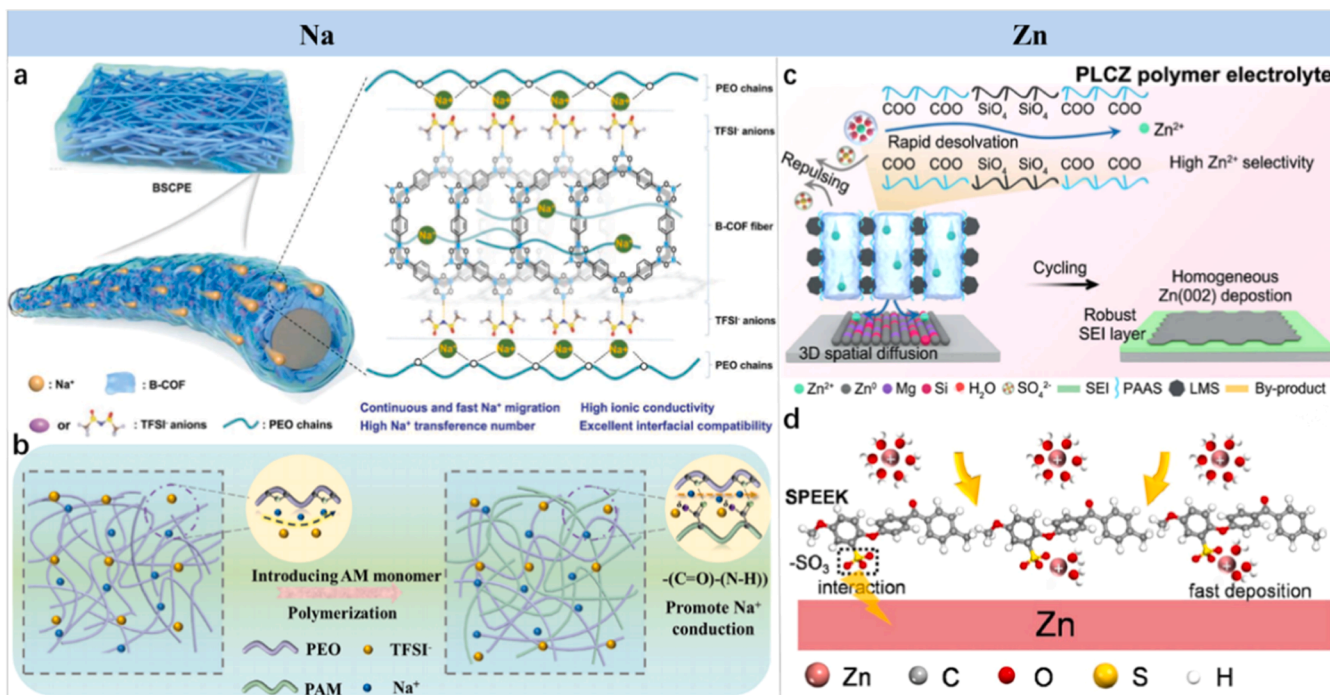


Fig. 16. a) The B-COF network not only reduces the crystallinity of PEO but also captures anions, thereby accelerating Na⁺ transport. Reproduced with permission [251]. Copyright 2024, Wiley-VCH. b) Schematic illustration of the in-situ polymerized AM monomers within the PEO/PAM scaffold. Reproduced with permission [252]. Copyright 2024, Wiley-VCH. c) Schematically illustrating the Zn deposition in the multifunctional QSPE. Reproduced with permission [253]. Copyright 2025, Springer Nature. d) Zn²⁺-SPEEK is constructed on the zinc metal anode, providing coordination sites to guide the uniform deposition of Zn²⁺. Reproduced with permission [254]. Copyright 2022, Elsevier.

commonly used plasticizer. However, it exhibits poor reduction stability and is prone to side reactions with sodium metal, leading to irreversible corrosion of the anode [249]. Fortunately, polymer chains abundant in ester groups exhibit strong van der Waals interactions with free SN molecules, effectively serving to immobilize them. Building upon this foundation, Na^+ demonstrate dual transport behavior: they either rapidly diffuse within the SN phase through its solvation sheath structure or coordinate with $\text{C}=\text{O}$, thereby establishing supplementary migration pathways [250]. To avoid unnecessary troubles caused by the introduction of solvents into polymer electrolytes (such as leakage, evaporation, and interfacial side reactions), Guo et al. selected to introduce a boron-containing COF into PEO [251]. The decrease in PEO crystallinity and the effective "capture" of anions by B in COF jointly facilitate the migration of sodium ions. As illustrated in Fig. 16a, the liberated free Na^+ subsequently coordinated with the EO groups on the accelerated PEO chains, significantly enhancing ionic mobility. Ma et al. also incorporated acrylamide (AM) monomers into PEO and formed an interpenetrating PEO/PAM network via in-situ polymerization, as shown in Fig. 16b [252]. The key advantage lies in the coordination interactions: the $\text{C}=\text{O}$ groups in PAM's amide moieties coordinate with Na^+ , while the $-\text{NH}$ groups bind to TFSI^- anions, synergistically promoting the dissociation of NaTFSI . With TFSI^- immobilized by $-\text{NH}$ groups, the interpenetrating network establishes a "dissociation-transport-relay" pathway for Na^+ migration. Consequently, the Na^+ transference number increased from 0.18 in pure PEO to 0.65 in the PEO/PAM composite.

In fact, many of the coordination mechanisms previously introduced for lithium rechargeable batteries hold significant reference value for sodium rechargeable batteries. Future research on coordination mechanisms in sodium rechargeable batteries should prioritize the development of novel ligands with high selectivity and strong coordination capacity for Na^+ , as well as explore their applications at the cathode interface. Meanwhile, leveraging theoretical calculations and advanced characterization techniques to deeply elucidate the structural evolution of sodium ion solvation sheaths will provide a solid theoretical foundation for designing optimized electrolyte systems.

5.2.2. Coordination chemistry of polymer-based electrolytes in zinc batteries

In zinc batteries, the use of polymer-based electrolytes to regulate the solvation structure of zinc ions (Zn^{2+}) through coordination interactions has become a widely adopted strategy. Owing to the strong coordination interaction between Zn^{2+} and ligands, a moderate amount of water is generally introduced to lower the migration barrier of Zn^{2+} . In this process, functional groups on the polymer chains help modulate the solvation structure of hexahydrated Zn^{2+} , reduce the content of active water, and thereby effectively suppress issues such as hydrogen evolution and corrosion [255]. For example, Yang et al. designed a multifunctional QSPE composed of three synergistic components linked via molecular crosslinking (Fig. 16c) [253]. The introduction of sodium polyacrylate (PAAS) with $-\text{COO}^-$ groups and lithium magnesium silicate (LMS) with anisotropic charge distribution effectively replaces some of the coordinated water molecules around Zn^{2+} , transforming the solvation structure into $[\text{Zn}(\text{H}_2\text{O})_3(\text{COO})\text{LMS}]^+$. Lee et al. designed a zwitterionic GPE based on sulfobetaine methacrylate (SBMA) [256]. As the polymer matrix, SBMA features negatively charged $-\text{SO}_3^-$ groups on its chain segments, which serve as preferential coordination sites to strongly bind Zn^{2+} and guide their uniform distribution, forming directional transport channels. The strong coordination capability of $-\text{SO}_3^-$ enables it to directly enter the solvation sheath of Zn^{2+} , partially replacing water molecules originally coordinated with Zn^{2+} . Meanwhile, the positively charged cationic quaternary ammonium groups exert electrostatic repulsion to effectively suppress the disordered diffusion of Zn^{2+} on the electrode surface.

In addition, constructing an artificial interfacial protective layer represents another effective strategy [257,258]. Analogous to LIB,

pre-forming a coordination-site-rich artificial protective layer (e.g., COF, functional polymers) on the zinc anode surface can function as an "ion sieve." This protective film effectively excludes water molecule interference while providing uniform migration pathways for Zn^{2+} , guiding its planar deposition. Consequently, this approach simultaneously addresses the two major challenges of dendrite growth and corrosion. Fan et al. also fabricated a Zn^{2+} ion-exchanged sulfonated poly(ether ketone) (Zn^{2+} -SPEEK) conductive film on the Zn anode surface (Fig. 16d) [254]. The abundant $-\text{SO}_3^-$ groups on the film surface provide Zn^{2+} coordination sites, promoting uniform deposition and suppressing dendrite growth.

Solid-state ZIB have attracted extensive attention in recent years due to their avoidance of challenges associated with aqueous electrolytes [259,260]. Liu et al. identified the ligand 2,6-bis((propylimino)methyl)-4-chlorophenol (Hbimcp) and introduced it into poly(propylene oxide) polymer chains to prepare a SPE [261]. This ligand contains two identical nitrogen atoms. However, due to steric hindrance, they cannot coordinate with the same Zn^{2+} simultaneously. Such unstable monodentate coordination allows Zn^{2+} to rapidly exchange positions between different ligands, enabling intramolecular and intermolecular migration. This rapid dynamic coordination not only facilitates efficient Zn^{2+} conduction but also endows the material with self-healing capability. Nowadays, developing zinc rechargeable batteries based on non-aqueous and deep eutectic solvent systems, while leveraging coordination chemistry to regulate their internal environments, represents a critical approach to overcoming the voltage window limitations of aqueous batteries and enhancing energy density. Although coordination chemistry has demonstrated unique and pivotal roles in addressing issues such as hydrogen evolution and corrosion in aqueous ZIB, the field still faces numerous challenges and opportunities. For instance, concerns include the oxidative decomposition of coordinating molecules and the reversibility of coordination reactions. Of course, these challenges also define clear research directions for the future. The process of overcoming these obstacles constitutes the key to advancing zinc batteries from fundamental research to practical applications.

5.2.3. Coordination chemistry of polymer-based electrolytes in other rechargeable batteries

Coordination chemistry, as a pivotal approach for regulating ion transport behavior and interface stability, extends its applications far beyond lithium-based batteries, sodium-based batteries, and zinc-based battery systems. In response to the growing demands for diversified energy storage solutions, a series of emerging rechargeable battery systems based on more abundant, lower-cost, or theoretically higher-energy-density metals or nonmetals (e.g., potassium, calcium, magnesium, and fluorine) have garnered significant attention [262,263]. However, these systems face severe kinetic and thermodynamic challenges due to the unique physicochemical properties of their carrier ions (e.g., the relatively large ionic radius of K^+ and Ca^{2+} , the high charge densities of Mg^{2+} and F^-). This section focuses on these challenges, emphasizing recent advancements in coordination engineering to address critical issues such as interfacial chemical instability in potassium-based batteries, sluggish ion migration kinetics in magnesium-based batteries and calcium-based batteries, and the poor dissociation of fluoride salt in fluorine-based batteries. By elucidating universal design principles in coordination chemistry, this discussion aims to refinedly provide novel insights for the development of future emerging rechargeable battery technologies.

Like sodium metal, potassium metal offers core advantages of abundant resources and low cost. The exceptionally low negative potential of the K/K redox couple is also satisfied [264,265]. However, the ionic radius of K^+ (1.38 Å) is even larger than that of Na^+ , necessitating a higher CN of 7–9 to form irregular polyhedral coordination environments [266,267]. This starkly contrasts with the regular tetrahedral (LiO_4) or octahedral (LiO_6) coordination commonly observed for Li^+ . Furthermore, interfacial chemical instability remains a critical challenge

for all-solid-state potassium-ion batteries (PIB) [268,269]. Typically, Wu et al. employed $\text{Al}(\text{OTf})_3$ as a catalyst to initiate the ring-opening polymerization of 1,3-dioxolane, while introducing SN to reduce the length of polymer chains [270]. As depicted in Fig. 17a, K^+ coordinate with the O atoms on the polymer chains and move along with the chain segments. Compared to long chains, short chains are more conducive to the rapid migration of potassium ions, thereby enhancing ionic conductivity. Moreover, the short-chain structure mitigates interfacial polarization and improves the interfacial charge transfer rate. Nevertheless, unresolved issues such as interfacial chemical instability at the anode side and poor contact with the SPE persist, representing key obstacles in current PIB research.

Due to the high charge density of divalent Mg^{2+} , their transport in SPE is also severely hindered, resulting in generally low ionic conductivity and Mg^{2+} transference number [271,272]. In this context, CGPE may offer a more promising alternative. Sun et al. selected polyethylene glycol (PEG), a polymer with long chain segments, dissolved it in tetrahydrofuran (THF), and added magnesium salt to form a CGPE through in situ polymerization (Fig. 17b) [273]. PEG's stronger coordination with Mg^{2+} partially replaces THF in the solvation sheath, promoting interfacial desolvation. Its $-\text{OH}$ groups further coordinate with anions, restricting their motion and suppressing concentration polarization, which raises the Mg^{2+} transference number to 0.74. Nevertheless, the high charge density of Mg^{2+} still limits overall ionic conductivity.

Calcium, another divalent metal, exhibits a lower redox potential and greater resource abundance compared to magnesium [274,275]. Furthermore, its relatively lower charge density favors improved transport and diffusion [276,277]. Shinohara et al. designed a GPE by using $\text{Ca}(\text{BH}_4)_2$, LiBH_4 , and PTHF (as shown in Fig. 17c) [278]. The

addition of lithium salt with the same anion did not alter the cross-linking and solidification. Li^+ competed with Ca^{2+} for coordinating with THF molecules, significantly reducing the solvation energy of Ca^{2+} . Meanwhile, due to the lower charge density and greater coordination flexibility of Ca^{2+} , this GPE exhibited superior electrochemical performance compared to the previously reported Mg-based GPE which used a similar design concept [279]. Similarly, Pathreker et al. developed a GPE based on poly(vinylimidazole) [280]. The nitrogen atoms of the imidazole groups coordinate weakly with the Ca^{2+} , effectively lowering the migration energy barrier for Ca^{2+} . Combined with the shorter intermolecular spacing among imidazole groups, this approach resolved the difficulty of low ionic conductivity in calcium-based batteries caused by strong coordination between Ca^{2+} and EO units. The developed GPE achieved a room-temperature ionic conductivity of $1.26 \times 10^{-4} \text{ S cm}^{-1}$, demonstrating that nitrogen-based heterocyclic groups are excellent alternatives to traditional oxygen-based ligands. This coordination strategy may also hold potential for application in magnesium-based batteries.

Fluoride ion batteries (FIB) exhibit exceptionally high theoretical capacity density (5000 Wh l^{-1}) and rely on abundant fluorine reserves in the Earth's crust [281,282]. Although the development of FIB is still in its infancy so far, there have been many remarkable research advancements. Yu et al. designed a SPE suitable for all-solid-state FIB [283]. As shown in Fig. 17d, The polymer matrix employs polyvinyl alcohol (PVA) rich in $-\text{OH}$ groups, which serve as coordination sites for F^- to facilitate its transport. Additionally, $\beta\text{-PbSnF}_4$ (PSF) was incorporated as an "ion pump" embedded within PVA chains. PSF functions as a Lewis acid site, accelerating the dissociation of CsF salt through a "push-pull" coordination effect—attracting F^- while repelling Cs^+ . Consequently, this SPE achieves a room-temperature ionic conductivity of $2.26 \times 10^{-4} \text{ S cm}^{-1}$.

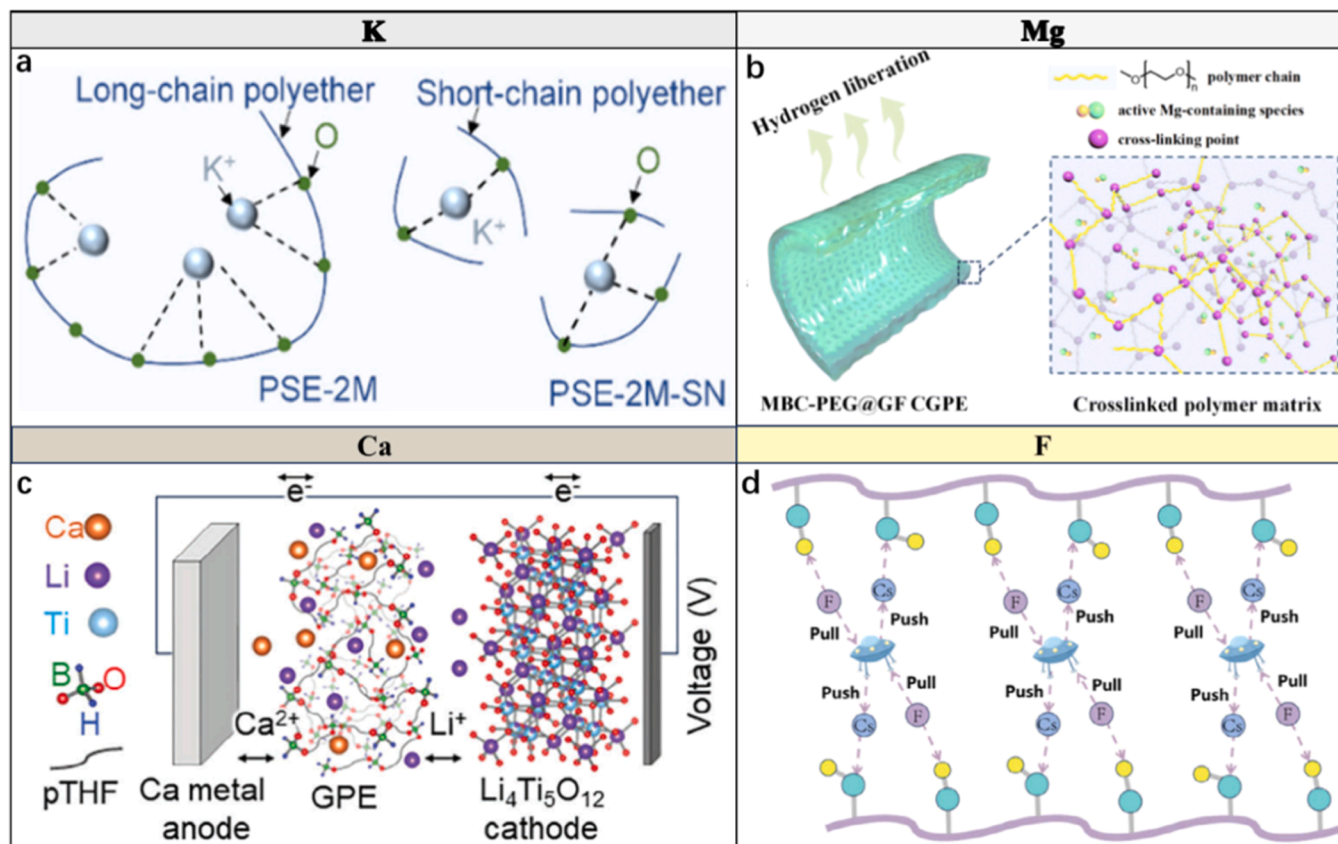


Fig. 17. a) Schematics of coordination of K^+ with long-chain polyether and short-chain polyether. Reproduced with permission [270]. Copyright 2025, American Chemistry Society. b) Schematic illustration of the synthesis pathway for the MBC-PEG@GF CGPE. Reproduced with permission [273]. Copyright 2025, Royal Society of Chemistry. c) Concept of dual-cation battery ($\text{Ca}||\text{GPE}||\text{Li}_4\text{Ti}_5\text{O}_{12}$). Reproduced with permission [278]. Copyright 2024, Wiley-VCH. d) Schematic diagram of "push-pull" effect of PSF in PVA polymer system. Reproduced with permission [283]. Copyright 2025, Wiley-VCH.

and an F^- transference number of 0.53. Unlike metal-ion batteries where carriers are cations, FIB utilize anions as charge carriers, necessitating distinct coordination design strategies. The role of Lewis acid-base chemistry is reversed: in contrast to Li^+ systems, F^- acts as a Lewis base requiring coordination with Lewis acid sites. Thus, SPE design for FIB must incorporate Lewis acid sites, with core ligands considering hydrogen atoms in polymers (e.g., from $-OH$) and metal cations in fillers or anodes (e.g., Sn^{2+} , Pb^{2+}) [284]. Meanwhile, we hope to conduct F^- in the interface layer and immobilize cations rather than anions.

In summary, coordination chemistry strategies, successful in lithium battery polymer electrolytes, are increasingly being explored for other secondary batteries. However, due to the larger ionic radii and stronger coordination interactions with functional groups in these systems, ion migration remains challenging, often still requiring solvent assistance to achieve sufficient conductivity. Moving forward, more sophisticated coordination design strategies are needed to advance the coordination chemistry of polymer-based electrolytes, particularly for all-solid-state systems, in these alternative battery chemistries.

6. Summary and perspective

As the core framework for the design of polymer-based electrolytes, coordination chemistry runs through multiple systems including SPE, QSPE, GPE, and CPE. By precisely regulating the CN, coordination strength, and coordination mode between Li^+ and components such as polymer chains, plasticizers, and inorganic fillers, researchers have successfully achieved synergistic enhancements in ionic conductivity, transference number, mechanical strength, and interfacial stability (Fig. 18). From the early PEO-based electrolytes to the recently developed strategies such as weak solvation structures, multidentate coordination, and anion immobilization, the understanding of coordination mechanisms has continuously evolved, providing a theoretical foundation and practical pathway for the realization of high-performance solid-state batteries.

Although remarkable progress has been achieved in the research of polymer-based electrolytes based on coordination chemistry, numerous challenges and opportunities remain. Future studies can be further expanded and deepened in the following four directions.

6.1. Application and design of new coordination mechanisms

Building upon existing well-established coordination applications, it is imperative that we gain a deeper understanding of coordination mechanisms and develop novel coordination strategies. For instance, the

design of dynamic and reversible coordination bonds, along with the development of stimuli-responsive coordination systems (e.g., those responsive to light, heat, or electric fields), can enable intelligent regulation of ion transport channels. By leveraging the reversibility of coordination bonds, "smart electrolytes" capable of adaptively adjusting coordination strength during charge-discharge cycles can be developed to meet performance requirements under various operating conditions. However, the current design of coordination chemistry-based polymer electrolytes still largely relies on empirical trial-and-error approaches. Integrating ML models with high-throughput computation can facilitate the prediction of better coordination pairs and coordination environments, thereby accelerating the development of new materials. Compared with conventional trial-and-error approaches, utilizing AI and predictive modeling offer a more efficient route to screen promising coordination functional groups, polymer matrices, and electrolyte formulations. In particular, establishing shareable databases that integrate key coordination descriptors (e.g., binding energy, CN, segmental dynamics, and interfacial compatibility) would enable the construction of quantitative structure-property relationships. Such an approach could significantly improve the efficiency of electrolyte design and accelerate the development of polymer-based electrolytes for practical solid-state battery applications.

What's more, it is essential to deepen the concept of multiple synergistic coordination by constructing multi-metal center systems (e.g., bimetallic or multimetallic coordination nodes) or mixed ligand systems, leveraging synergistic effects to optimize ion transport and interfacial stability. Additionally, cross-disciplinary collaborative innovation holds paramount importance. For instance, by drawing inspiration from the sophisticated structures of ion channels in biological systems (e.g., ion-selective channels), biomimetic coordination environments can be designed to achieve highly selective ion transport.

6.2. Cross-system application expansion

Multivalent ions such as Zn^{2+} , Mg^{2+} , and Al^{3+} exhibit strong ion-ion interactions due to their high charge densities, posing dual challenges for polymer-based electrolytes in terms of severe ion pair association and high interfacial desolvation energy barriers. By extending coordination mechanisms to multivalent ion battery systems, issues specific to these systems, such as sluggish ion transport and dendrite growth, can be addressed through ligand design and coordination environment optimization. For instance, designing multidentate coordination sites can weaken electrostatic binding between multivalent ions and counterions/solvents via charge delocalization. Additionally, constructing

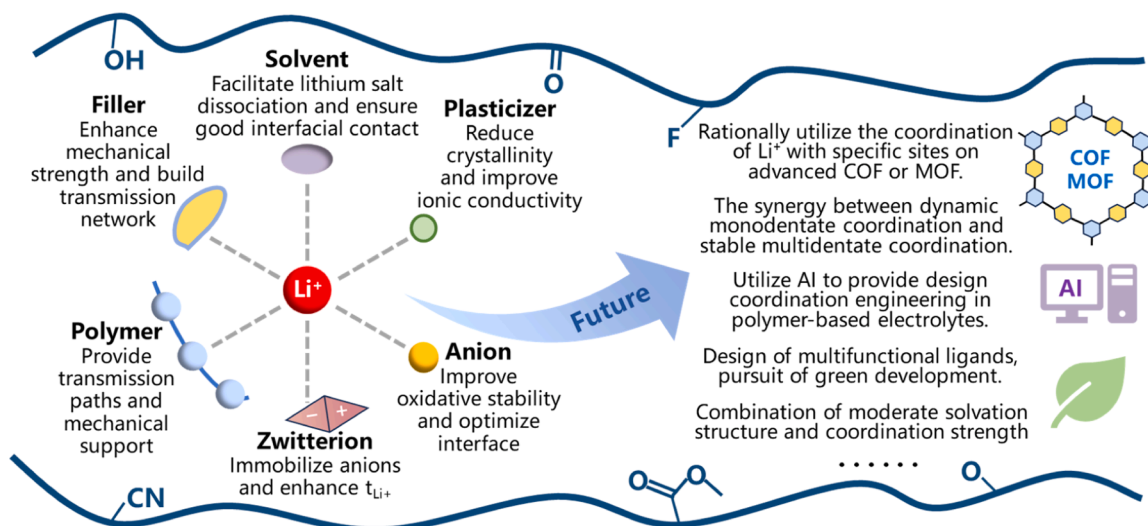


Fig. 18. The application of coordination in polymer-based electrolytes and the future development directions.

dynamic coordination networks (e.g., reversible complexation) enables a "coordination-decoordination" cycle at interfaces, thereby reducing desolvation energy barriers and suppressing side reactions. Grasping coordination mechanisms as a "universal key" not only facilitates ion pair dissociation but also promotes the exploration of coordination chemistry applications in energy storage and conversion systems beyond solid-state batteries, including supercapacitors, fuel cells, and electrocatalysis.

6.3. Industrialization and practicality perspective

In the industrialization research of lithium rechargeable batteries, both practicality and safety are critical issues that must be addressed. Although polymer-based electrolytes designed based on coordination chemistry demonstrate exceptional performance in laboratory settings, their transition from "academic materials" to "market products" still faces numerous formidable challenges. Cost stands as one of the primary obstacles to industrialization. Numerous high-performance polymer systems reported in the literature often rely on expensive raw materials and complex synthetic routes. While fundamental polymers such as PEO are inexpensive and widely available, this is not the case for numerous advanced functional polymers. The long-term, stable, and large-scale supply of their precursors remains a matter of debate. Rather than deliberately synthesizing monomers with complex structures, it is feasible to achieve unique coordination interactions and collaboratively construct an ideal solvation environment and ion transport channels by understanding the polarity, coordination mechanisms, and interactions with other ions of the most fundamental characteristic functional groups. Even simple polymers, cheap salts, and low-cost additives can engage in such interactions. This strategy shifts the complexity from the covalent synthesis of precursors to the supramolecular coordination assembly process, potentially leading to a significant reduction in overall costs.

Furthermore, traditional laboratory methods for preparing polymer-based electrolytes, such as prolonged high-pressure hot pressing, are ill-suited for industrial-scale roll-to-roll slurry coating processes. Polymer-based electrolytes must not only exhibit high ionic conductivity and a sufficiently high modulus to inhibit dendrite growth, but also possess adequate mechanical flexibility and ductility to withstand the winding and stacking processes without fracturing. Against this backdrop, coordination engineering design offers unique advantages. By constructing network structures that combine strong and stable cross-linking points (e.g., multidentate chelation) with dynamic reversible bonds (e.g., monodentate coordination), it is possible to fabricate electrolyte films that combine structural robustness with processing adaptability.

Equally critical is the fact that most reported results are based on coin cells employing low-loading cathodes ($<2 \text{ mAh cm}^{-2}$) and excess lithium metal anodes, conditions that are far removed from commercial requirements. Practical solid-state batteries must be compatible with high-loading cathodes ($>4 \text{ mAh cm}^{-2}$), ultrathin lithium foils ($<50 \text{ }\mu\text{m}$), and operate stably over a wide temperature range ($-40 \text{ }^{\circ}\text{C}$ to $80 \text{ }^{\circ}\text{C}$). The significant volume changes that occur in thick electrodes during cycling pose a severe challenge to interface integrity. It has become imperative to utilize coordination chemistry to design polymer-based electrolytes with self-healing capabilities; address interface issues through precise regulation of anion coordination behavior and Li^{+} solvation structures; and further investigate the temperature-responsive characteristics of coordination bonds. To advance toward industrialization, an overall design approach is urgently needed: coordination chemistry should not only serve to optimize ion transport performance but also become a core tool for overcoming multiple bottlenecks related to cost, manufacturing, and practical application.

6.4. Green and environmental protection

On the path toward industrialization, adherence to green and

environmentally sustainable principles is imperative. The conventional preparation and recycling processes of liquid electrolytes involve substantial use of volatile and toxic organic solvents (e.g., DMF, and carbonate esters) and fluorine-containing lithium salt (e.g., LiPF_6 , which is prone to hydrolysis, generating HF), posing risks of leakage and volatilization that threaten both ecosystems and human health. Even in the realm of solid-state batteries, the synthesis of polymer-based electrolytes frequently relies on petroleum-based monomers, whose non-biodegradability—coupled with improper disposal of spent batteries—contributes to persistent microplastic and heavy metal pollution, which cannot be overlooked.

To address these issues, exploring natural polymers such as cellulose, chitosan, and lignin, or biodegradable polyesters, as matrix materials for polymer-based electrolytes (which contain abundant coordinable functional groups for constructing ion transport channels) offers a promising solution. This approach reduces reliance on fossil resources while mitigating long-term pollution from spent batteries. Additionally, designing specific coordination sites can enhance the intrinsic stability of electrolytes (minimizing decomposition products), enabling controlled degradation and component separation under mild conditions. Looking ahead, integrating green design principles deeply into the molecular design and synthesis processes of electrolyte materials to achieve a harmonious balance between high performance and environmental friendliness represents an inevitable and essential pathway for advancing lithium-based battery technologies toward true sustainability.

7. Conclusion

In conclusion, this comprehensive review establishes a coherent framework that bridges molecular-level coordination chemistry to the macroscopic performance of polymer-based electrolytes for solid-state batteries. We have elucidated how the rational design of coordination environments—encompassing strength, number, and denticity—serves as the fundamental lever to modulate ion transport dynamics, transference number, and interfacial stability across various electrolyte systems, from classic PEO-based SPE to advanced QSPE, GPE, and CPE. By systematically examining strategies such as competitive coordination with heterometallic ions or organic cations, polymer functionalization with charged/zwitterionic groups, and solvation structure engineering, this work consolidates key insights for decoupling ion conduction from polymer segmental motion and constructing stable interfaces. The discussed advancements, including anion coordination harnessing, high-entropy design, and AI-guided exploration, collectively chart a path from empirical discovery toward a unified blueprint for next-generation electrolyte design. The underlying coordination principles, as evidenced by their emerging applications in sodium-, zinc-, and other multivalent-ion batteries, further demonstrate their universality as a powerful design toolkit beyond the lithium-based systems. Ultimately, mastering coordination chemistry provides the critical link to achieving the long-sought synergy of high ionic conductivity, superior mechanical properties, and exceptional electrochemical stability, paving the way for the practical realization of high-energy, safe all-solid-state batteries.

CRedit authorship contribution statement

Fangqi Zhan: Writing – original draft, Methodology, Investigation, Conceptualization. **Tong Wu:** Investigation, Data curation. **Yingjie Wang:** Data curation. **Wenqing Sun:** Investigation. **Yuxiang Bai:** Investigation. **Kaiyang Zhang:** Data curation. **Pengfei Huo:** Investigation. **Jitao Huang:** Methodology. **Zhong Jin:** Writing – review & editing, Supervision. **Wen-Yong Lai:** Writing – review & editing, Supervision. **Qian Wang:** Writing – review & editing, Supervision, Resources. **Shi Wang:** Supervision.

Declaration of competing interest

The authors declare no competing interests.

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Data availability

No data was used for the research described in the article.

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